# Electronically stimulated sputtering and luminescence from solid argon

# C. T. Reimann

School of Engineering and Applied Science, University of Virginia, Charlottesville, Virginia 22901 and AT&T Bell Laboratories, Murray Hill, New Jersey 07974

# W. L. Brown

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

# R. E. Johnson

# School of Engineering and Applied Science, University of Virginia, Charlottesville, Virginia 22901 (Received 27 February 1987; revised manuscript received 12 June 1987)

Electronic excitation of condensed-gas solids by MeV light ions results both in luminescence and in kinetic ejection of atoms and molecules from the surface of the solid. This work reveals that ejection of Ar atoms from electronically excited solid argon films arises from two nonradiative repulsive dissociation steps in the deexcitation decay sequence which contains the major radiative transition. A hole-diffusion model with nonradiative quenching at the metal substate on which the films are grown accounts for the dependence of the sputtering and luminescence on film thickness and gives an estimate of 230 Å for the hole-diffusion length. The hole-diffusion model also explains the nearly linear dependence of the sputtering and luminescence yields on electronic stopping cross section for high-velocity incident ions. Intentionally added O<sub>2</sub> and N<sub>2</sub> impurities reduce the hole-diffusion length. These reductions provide values for effective reaction volumes,  $k_+ \tau_+$ , of  $7 \times 10^{-21}$  cm<sup>3</sup> for O<sub>2</sub> and  $3 \times 10^{-21}$  cm<sup>3</sup> for N<sub>2</sub>, where  $k_{+}$  is the interaction rate constant of the holes with the impurity and  $\tau_+$  is the lifetime of holes in pure films. The O<sub>2</sub> and N<sub>2</sub> impurities also quench nonmobile luminescent excimers,  $Ar_2^*$ , over large distances: 21 Å for O<sub>2</sub> and 11 Å for N2. The magnitude of the sputtering yield characterizes the vacuum interface as primarily hole reflecting, but with a surface-hole-trapping rate about 6 times that of the bulk. Surface  $O_2$  impurity greatly enhances surface trapping of free holes. Sputtering of  $Ar_2^*$  dimers is evident from the observation of 11.3-eV luminescence in the region in front of the argon films. The dimers are emitted with  $\sim 0.8$  eV of kinetic energy. This is consistent with the repulsive decay forming an energetic Ar<sup>\*</sup>, which forms  $Ar_2^*$  upon exiting or, possibly, the ejection of an  $Ar_2^*$  during trapping at the surface.

## I. INTRODUCTION

In this paper, MeV light-ion-induced sputtering (erosion) and luminescence of solid argon films is studied in order to determine the mechanisms of atomic ejection due to the electronic excitations and ionizations are produced. Electronic "potential" energy must be converted into kinetic energy of sputtered particles, and mechanisms for accomplishing this are not well understood. Because the initiating events are electronic excitations these mechanisms will also be related to those for electron- and photon-stimulated desorption.

Electronically induced sputtering is distinct from sputtering by elastic collisions, which is described by a collision cascade model.<sup>1,2</sup> In this model, a sequence of wide-angle momentum-transferring collisions starting with a collision between the incident ion and a target atom eventually results in atomic ejection. This model adequately explains the size of the sputtering yields of keV heavy ions incident on amorphous metal targets.<sup>3</sup> Bombardment of certain insulating films by swift light ions leads to erosion rates that are much higher than predicted based on the collision cascade theory. This was first noticed for keV light ions incident on KCl (Ref. 4) and for MeV light ions incident on low-temperature  $H_2O$  films.<sup>5</sup> The importance of electronically deposited energy in causing erosion was subsequently demonstrated for a variety of insulating films.<sup>6</sup>

The general nature of those processes leading to the electronic sputtering of insulators has been discussed.<sup>7,8</sup> However, in many cases that have been studied, the complicated chemistry of ion-induced fragments inhibits the interpretation of the results in terms of specific excitation and ejection mechanisms. For example, bombardment of D<sub>2</sub>O films with 1.5-MeV He<sup>+</sup> ions gives rise to an  $O_2$  yield which rises slowly with fluence, but a  $D_2O$ yield which is prompt on the fluence scale. This suggests the diffusion and interaction of fragments to form O<sub>2</sub> which is later sputtered.<sup>9</sup> Also, bombardment of CO films with 30 keV Kr<sup>+</sup> results in a variety of ejecta: CO,  $CO_2$ ,  $O_2$ , O,  $C_2$ , and  $(CO)_2$ , as well as in the subsequent creation of a carbon-rich residue.<sup>10</sup> In both of these examples, the varied composition and the rich transient behavior of the ejecta indicate the importance of fragment chemistry, but scant light is shed on ejection mechanisms. For the present study, solid argon was chosen be-

37 1455

cause of its monatomic van der Waals lattice. The behavior of ion-induced fragments is not a problem as it is with frozen films of molecular gases, and the results of excitation and ionization in the argon lattice are expected to be relatively simple compared to the case of condensed molecular gas solids.

It is well known that a consequence of electronic excitation of liquid and solid argon is the production of intense ultraviolet luminescence.<sup>11</sup> The luminescence spectrum is surprisingly rich and has been attributed to radiative decay of several types of excited centers.<sup>12</sup> The large Stokes shifts between optical-absorption and emission spectra are indicative of the large lattice relaxation in these excited centers. For example, the dominant 9.8-eV luminescence is produced as a result of a minimum electronic excitation of 12 eV to form Ar\*, an exciton. The Ar\* relaxes with a ground-state Ar atom to form an excimer  $Ar_2^*$  in which the internuclear separation is considerably smaller than the normal lattice spacing. Furthermore, this dimer is contained within a distorted cavity,<sup>12</sup> with the atoms nearest the dimer displaced outwards from their normal lattice positions by a distance of the order of 1 Å. Since the relaxation of electronic energy to form the luminescent center involves physical rearrangement of the lattice, considerable potential energy is stored in the center until it luminesces, at which time some portion of the lattice distortion energy can become available as kinetic energy of atoms. In previous works simple repulsive dimer decay models have been proposed to account for particle ejection.<sup>13-15</sup> In one of these,<sup>13</sup> conversion of electronic excitation to kinetic energy of atomic motion is attributed to two separate repulsive steps involving  $Ar_2^+$  and  $Ar_2^*$ dimers, one of which occurs before and the other after radiative decay yielding 9.8-eV photons. Another model<sup>16</sup> attributes ejection to the distortion produced around a dimer near the surface as dimer formation and relaxation take place (cavity ejection). These models imply a correlation between sputtering and luminescence in electronically excited argon films. The present work examines this correlation in detail, considerably elaborating on our previously published work.<sup>17-19</sup>

This paper presents the experimental observations of sputtering and luminescence from argon films bombarded by MeV light ions. A simple relationship is found between the dependencies of the sputtering yield of argon atoms and the 9.8-eV luminescence yield on the thickness of the argon film. This relationship is modeled from diffusion and decay of electronically excited states and provides the value of the diffusion length of Ar<sup>+</sup> ions (holes). The dependence of sputtering and luminescence on the excitation density along the track of individual exciting H and He ions is examined by changing the ion energy over a wide range. The yields are nearly linear in the excitation density and reveal the low probability of interaction of holes with each other as they diffuse in the lattice. The sputtering and 9.8-eV luminescence correlation leads to evaluation of the boundary conditions for holes at the metallic substrate on which the film is grown. The data are consistent with this interface being a perfect sink. The absolute magnitude of the sputtering yield is additionally accounted for by the model and provides an estimate of the boundary conditions for holes at the vacuum interface of the film. In an uncontaminated film this interface is found to be highly reflecting for diffusing holes. The influence of intentionally added impurities on both luminescence and sputtering yields is also examined. These dependencies lead to values for reaction-rate constants or cross sections between the excited states of argon atoms and impurity centers. Luminescence at 11.3 eV is found to be directly correlated with sputtering, both having the same film thickness dependence. The luminescence is present in a plume of sputtered particles in front of the bombarded target.

### **II. EXPERIMENT**

Figure 1 shows a schematic diagram of the experimental setup for measuring sputtering and luminescence from ion-bombarded argon films. The experiments were done in a stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of 1 to  $3 \times 10^{-9}$  Torr, maintained with a cryopump. The quadrupole mass spectrometer is in a separate UHV chamber closely coupled to the first but separately pumped with a second cryopump. The uv spectrometer is in a third chamber which is vacuum isolated by a  $0.58 \times 8$ -mm<sup>2</sup> slit which also serves to define the region at the target from which



VACUUM MONOCHROMATOR

FIG. 1. Experimental apparatus for measuring sputtering and luminescence from ion-bombarded solid argon films. The inset shows the grazing angle target geometry used in studying uv emission from a plume in front of the target. See Fig. 7 and discussion in Sec. III B. light is observed by the spectrometer. In some experiments in which only photons with energy < 11 eV were being studied, the slit was replaced by a MgF<sub>2</sub> window.

Films of frozen argon were created by directing room-temperature argon gas towards a beryllium foil onto which a 50-Å gold overlayer had been evaporated. The beryllium was mounted on a copper cold finger cooled by a liquid-helium transfer system. The temperature of the cold finger was  $\sim 12$  K as measured by a Chromel-Au-Fe thermocouple referenced to an ice bath. The inlet gas came from a stainless-steel manifold which had bottles of pure gas attached to it. Commercially available argon gas with a stated purity of 99.9995% was used. The gas pressure in the manifold was measured with a capacitance manometer. With suitable calibration (discussed below), a change in pressure in the manifold, which had a fixed volume of  $\sim 100$  cm<sup>3</sup>, could be converted into an absolute film thickness on the cold finger. All films were grown at the same continuous rate by adjusting a leak valve to a maintain an argon partial pressure reading of  $\sim 3 \times 10^{-7}$  Torr on the ice chamber ionization gauge as the manifold pressure decreased. The argon partial pressure near the target during film growth is considerably higher than the chamber pressure, since in the usual film growth geometry, most of the admitted argon directly encounters and sticks to the target. Under these conditions, it took about 200 s to grow a film 2000 Å thick. This growth procedure insured that, in a series of runs, the co-deposition of residual impurity gases from the UHV system was small and constant at less than 0.1%.

Some of the argon films were deliberately "doped" with small amounts of O2 or N2, up to concentrations of 1%. These films were created by admitting a mixture of argon and the impurity towards the cold target. The sticking probability for all species on the cold finger is sufficiently high that the as-grown film impurity was expected to be the same as the impurity concentration in the manifold, which is accurately known based on the partial pressures in the manifold. A variety of checks verified this expectation. Surface impurity experiments were done by exposing an argon film to several langmuirs (L) of  $O_2$ . (In these experiments, the impurity was admitted diffusely rather than directly at the target, so that 1  $L \approx 1$  monolayer.) To remove a film, the cold finger was heated to  $\sim 40$  K using a built-in resistive heater.

The frozen films were bombarded by MeV light ions obtained from a 3.75-MeV van der Graaff accelerator. The measurement of ion beam current is crucial to calculating sputtering and luminescence yields, but doing this reliably is difficult<sup>20</sup> due to large yields of secondary electrons from the target and uv photons from the target which produce photoelectrons at other metal surfaces in the chamber. The suppression scheme used in the present work consisted of two (mostly) solid cans concentrically surrounding the target. The outer can was held at -644 V, the inner can at +74 V with respect to the target. The ion beam current was read as the sum of the current to the target and those two surrounding cans. The accuracy of this current integration scheme

was  $\sim 4\%$  or better.

Absolute sputtering yields and argon film thickness calibrations were obtained by Rutherford backscattering spectrometry (RBS).<sup>21</sup> For the RBS measurements, 1.5-MeV He<sup>+</sup> ions were brought onto the films through a 1-mm-diam limiting aperture and the central hole of an annular solid-state particle detector. The backscattered ions were energy analyzed by the solid-state detector, and a computer system collected the resulting energy spectrum.

Figure 2 shows typical RBS spectra for bare Au-Be, a freshly grown Ar film, and for the Ar film bombarded by 1.5-MeV He<sup>+</sup>. The 50-Å gold layer of the target gives rise to a narrow peak at high backscattering energy. Because ions which backscatter from the gold pass through any overlying materials, they lose energy in accordance with the stopping cross section  $S_e$  of helium ions in whatever film lies on top of the gold. Therefore, a shift in energy position of the gold peak is quantitatively related to a change in the thickness of the film. If a shift in the gold peak is produced by application of a known ion fluence, an absolute sputtering yield (sputtered atoms per incident ion) may be calculated. If the shift is produced by growing a new film, the thickness of the film may be calculated and the gas inlet system thus calibrated. Under some conditions the gold centroid did not shift uniformly as the ion fluence increased, which indicated a fluence dependence of the sputtering yield. Part of this was related to the thickness dependence of sputtering to be discussed below, but part represented a change in the properties of the film. Also, the width of the gold peak was frequently an increasing function of ion fluence, indicating that the film was becoming nonuniform as it was eroded, a phenomenon noted in sputtering of other condensed gas films.<sup>5,22</sup>

Relative sputtering yields of neutral species were measured with a quadrupole mass spectrometer (QMS). QMS data were taken with CAMAC pulse-counting electronics run by a DEC PDP 11-23 minicomputer, a combination which acted as a versatile programmable



FIG. 2. RBS spectra measured during the erosion of an argon film by 1.5-MeV He<sup>+</sup>. As-grown ( $\Box$ ); fluence ~4.5×10<sup>15</sup> He<sup>+</sup>/cm<sup>2</sup> ( $\odot$ ); fluence ~9.3×10<sup>15</sup> He<sup>+</sup>/cm<sup>2</sup> ( $\odot$ ); bare target ( $\blacksquare$ ).

electronic strip chart recorder. The ion beam was switched on and off electronically by a computercontrolled pulser. The computer automatically switched the QMS between selected mass settings, and at each setting, it turned the beam on and then off. During both the on and off periods, the computer counted QMS pulses (signal on, signal off), giving a temporally local measure of both the ion-induced mass signal and the background at that mass setting. The ion beam dose (q)added to the film during each beam-on period was also recorded. (The dose is measured in "counts," where each count is  $10^{-11}$  C of charge collected on the target.) Then the relative sputtering (or luminescence) yield was [(signal on) - (signal off)]/q.

Typical raw data were taken using a measurement time per channel of 0.3 s, and a 1.5-MeV He<sup>+</sup> current in the range 2 to 10 nA through the 1-mm-diam defining aperture. If the pulsed beam was prevented from hitting the target for several seconds by closing a mechanical beam line shutter, the background observed was the same as that measured after the beam had been off for the 0.3-s data acquisition time. The signal-tobackground ratio was typically  $\sim 1$  at the largest current. In Fig. 3, the relative sputtering yield, (signal on-signal off)/q, is plotted as a function of fluence. Even though the measurements recorded in a group of channels near the center of the run were made at reduced beam current, the relative sputtering yield is the same as that of the rest of the run (although the larger scatter reflects the smaller signal-to-background ratio). This eliminates the possibility of collective effects such as "sputtering" by macroscopic beam heating, which would give rise to sputtering signals nonlinear in ion beam current.

Figure 3 shows that the sputtering yield had an initial spike (transient) which lasted for a fluence of  $\sim 5 \times 10^{12}$ ions/cm<sup>2</sup>. We ascribe this initial spike to surface contamination built up in the time between film deposition and the sputtering measurements. To assign a yield to

۳œ

õ 3 5 6 FLUENCE (IOI4 He Ions/cm2) FIG. 3. Fluence dependencies of relative yields. QMS sputtering yield  $(\bullet)$ ; spectrometer luminescence yield for

 $hv = 9.8 \text{ eV} (\odot).$ 

the data, the subsequent fluence dependence of the yield was extrapolated to zero fluence, ignoring the initial spike. The extra sputtering due to the initial spike removed only about a quarter of a monolayer of film. In many cases, there is a gradually decreasing sputtering yield as the ion dose increases as noted above in connection with the RBS measurements.

Ion-induced luminescence from argon films was measured with a 0.2-m vacuum ultraviolet spectrometer. The dispersive element is an aberration-corrected concave holographic grating. The grating is coated with Al and has a  $MgF_2$  overlayer. Output pulses from either a phototube assembly with a uv-to-visible converter or from a channeltron were processed by the same software as QMS pulses. The dominant 9.8-eV luminescence band in pure argon films is  $\sim 0.5$  eV wide, and to look at the whole band at once, the monochromator slits were set to a width of 1.5 mm. To look at the spectral shape of the emission with higher resolution the monochromator slits were typically set to 0.5 mm.

Figure 3 shows the relative 9.8-eV luminescence yield plotted versus fluence. There is no evidence for an initial spike such as that observed in sputtering, and a yield is assigned to the data by extrapolating the yield versus fluence to zero fluence. For other luminescence bands, the fluence dependence was very different than that shown in Fig. 3 and will be discussed later.

To determine whether particles were sputtered in electronically excited states with resultant luminescence emitted from a plume of sputtered particles in the vacuum outside the solid, the target was viewed at at neargrazing angle (see inset of Fig. 1 and Fig. 7). With the entrance slit of the monochromator set at 0.5 mm and the 0.58-mm differential pumping slit, the monochromator views a region 1.1 mm wide at the position of the target. The target could be translated perpendicular to the spectrometer axis which is defined by the two slits. The luminescence spectrum was obtained at different positions of the target; for example, with the monochromator looking at the region just outside the beam spot or directly at the beam spot.

## **III. EXPERIMENTAL RESULTS**

## A. Dependence of sputtering on ion stopping cross section

Solid argon films sputter very efficiency under electronic excitation by incident MeV light ions. For example, the sputtering yield  $Y_S$  of 1.5-MeV He<sup>+</sup> ions is ~42 atoms/ion. The dependence of  $Y_S$  on the electronic stopping cross section  $S_e$  is shown in Fig. 4. The present work has provided absolute  $Y_S$  obtained by RBS for 1.5-MeV He<sup>+</sup> and 1.5-MeV H<sup>+</sup>, and relative  $Y_S$  obtained with the QMS for He<sup>+</sup> in the energy range 1.0 to 3.0 MeV and  $H^+$  in the energy range 0.2 to 2.5 MeV. Relative  $Y_S$  values were also obtained for 1.0-MeV H<sub>2</sub><sup>+</sup> and 1.5-MeV  $H_3^+$  and selected energies of  ${}^{3}\text{He}^+$ . Relative  $Y_S$  were normalized to an absolute scale based on the absolute yield measured for 1.5-MeV He<sup>+</sup>. Also shown in Fig. 4 is a series of absolute  $Y_S$  obtained from Ref. 20 for He<sup>+</sup> in the energy range 1.3 to 3.0 MeV.





FIG. 4.  $S_e$  dependence of the sputtering and 9.8-eV luminescence yields. The solid lines are to guide the eye. Sputtering: QMS, H<sup>+</sup> ( $\oplus$ ); QMS, <sup>4</sup>He<sup>+</sup> ( $\bigcirc$ ); QMS, <sup>3</sup>He<sup>+</sup> ( $\oslash$ ); QMS, H<sub>2</sub><sup>+</sup> ( $\oplus$ ); QMS, H<sub>3</sub><sup>+</sup> ( $\oplus$ ); RBS, He<sup>+</sup>, and H<sup>+</sup> ( $\blacksquare$ ); RBS, <sup>4</sup>He<sup>+</sup>, Ref. 20 ( $\triangle$ ); RBS, <sup>3</sup>He<sup>+</sup>, Ref. 20 ( $\blacktriangle$ ). The QMS data were normalized to the absolute sputtering yield for 1.5-MeV He<sup>+</sup>. The 9.8-eV luminescence: H<sup>+</sup> ( $\oplus$ ); <sup>4</sup>He<sup>+</sup> ( $\bigcirc$ ); <sup>3</sup>He<sup>+</sup> ( $\oslash$ ); H<sub>2</sub><sup>+</sup> ( $\oplus$ ); H<sub>3</sub><sup>+</sup> ( $\oplus$ ).

Data for He<sup>+</sup> and H<sup>+</sup> are plotted at the appropriate tabulated  $S_e$ .<sup>23,24</sup> Data for  $H_n^+$  are plotted at *n* times the  $S_e$  for H<sup>+</sup> moving at the same velocity as the  $H_n^+$ . Data for <sup>3</sup>He<sup>+</sup> are plotted at  $S_e$  for <sup>4</sup>He<sup>+</sup> at the same velocity. For ions in the above energy ranges,  $Y_S$  is nearly proportional to  $S_e$ . This dependence is in contrast to the nearly quadratic dependence observed for a number of condensed molecular gas targets, H<sub>2</sub>O and CO, for example.<sup>25,26</sup>

#### **B.** Ion-induced luminescence

Solid argon films, in addition to sputtering efficiently, also luminesce in the far ultraviolet when electronically excited by fast ions and other ionizing radiation. Figure 5 shows a 1.5-MeV He<sup>+</sup>-induced spectrum in the (9-12)-eV photon energy range. Prominent features are noted at 9.8, 11.2, and 11.7 eV. The inset shows a published emission spectrum<sup>16,27</sup> in this same energy region, taken with higher spectral resolution for solid argon excited by 5-keV electrons. The resolution in the present work did not permit separation of the three spectral features between 11.5 and 12 eV. The feature labeled Wat ~11.3 eV in the inset was consistently measured in the present work to be at a slightly lower energy. It is not clear whether the discrepancy is significant. It will be assumed that the feature observed at ~11.2 eV in Fig. 5 is the W band of Refs. 16 and 27.

Broad luminescence bands at 6.2 and 7.6 eV were also found. These bands were enhanced by deliberate addition of  $O_2$  and  $N_2$ , respectively, to the films. These results are consistent with results published in the literature.<sup>28,29</sup> We believe the appearance of these bands in



FIG. 5. Ion-induced luminescence spectrum of pure argon between photon energies of 9 and 12 eV. The line is to guide the eye. The horizontal bar shows the resolution. The inset shows a high-resolution spectrum in the same energy range, from Ref. 16.

our purest films was due to incorporation of background gas impurities at less than 0.1% concentration as noted above.

The  $S_e$  dependence of the 9.8-eV luminescence yield  $(Y_{L,9.8 \text{ eV}})$  was measured for He<sup>+</sup> in the energy range 1.0 to 3.0 MeV, and for H<sup>+</sup> in the energy range 0.2 to 2.5 MeV. The results, as shown in Fig. 4, are even more nearly proportional to  $S_e$  than the sputtering yields. For fission fragments with  $S_e$  about an order of magnitude higher than the highest values covered in this work, the published ratio of  $Y_{L,9.8 \text{ eV}}$  to  $S_e$  eventually dropped relative to its nearly constant value at lower  $S_e$ .<sup>30</sup> The spectral features between 11 and 12 eV are also approximately linear in  $S_e$ .

The W-band luminescence at 11.2 eV seemed to come at least partly from a plume of sputtered particles in front of the ion beam spot, rather than completely from the beam spot. To observe this, the target was oriented to be nearly on edge with respect to the spectrometer entrance axis (see inset in Fig. 1). Then the target was translated very nearly perpendicularly to the axis of the uv spectrometer, and the W and 9.8-eV features were measured. The results are summarized in Fig. 6. The smaller the values of target translation y, the farther in front of the target the spectrometer looks. The W band is visible for a wide range of translation than the 9.8-eV



FIG. 6. Dependence of 9.8- and 11.2-eV luminescence yields on the spatial position of the beam spot with respect to the monochromator viewing axis. Normalized 9.8-eV luminescence ( $\bigcirc$ ); Normalized 11.2-eV luminescence ( $\square$ ). The wider spatial dependence of 11.2-eV luminescence than of 9.8-eV luminescence suggests that the 11.2-eV luminescence in part comes from a plume of sputtered particles.

band. If it can be assumed that 9.8-eV luminescence comes only from the beam spot then there is a plume of glowing sputtered particles that give rise to the luminescent feature W. The shapes of the translation dependences of the two spectral features are a consequence of the geometry, as summarized in Fig. 7. They have not been modeled quantitatively but we can conclude that the plume extends in front of the solid argon target between 0.1 to 1 mm. The peak of the W band was also observed to shift  $\sim 0.6$  eV lower in energy when the tip of the plume was observed. Therefore, our observation of the W band to be  $\sim 0.1$  eV lower than observed for the electron bombardment could be a result of a higher weighting of the plume contribution in our viewing geometry.

### C. Sputtering and luminescence film thickness dependences

A dominant feature of the sputtering of solid argon is the film thickness dependence of  $Y_S$ . An example of this for 1.5-MeV He<sup>+</sup> excitation is shown in Fig. 8. The solid line is the result of a fit to a model to be discussed below in Sec. IV. Practically identical sputtering thickness dependence shapes were obtained for 1.5-MeV He<sup>+</sup>,<sup>17</sup> 1.5-MeV H<sup>+</sup>,<sup>17</sup> and 0.75-MeV He<sup>+</sup> ions.<sup>20</sup> No difference was observed in the shapes of the thickness dependencies between QMS and RBS results.  $Y_S$  is smaller for thin films, and increases to a saturated value for film thicknesses of ~200 monolayers. Qualitatively similar sputtering thickness dependencies were reported for 1.0-MeV He<sup>+</sup> ions incident on solid Xe films<sup>31</sup> and for ions and electrons incident on neon films.<sup>32</sup>

The film thickness dependence of  $Y_S$  is not due to nonuniform excitation along the paths of the bombarding ions. The swift light ions used in the present work leave an essentially constant path of excitation and ionization throughout the depth of the film. However, saturating dependences of  $Y_S$  on film thickness have also been reported for the other extreme of excitation



FIG. 7. Detailed schematic of the plume experiment geometry. Depending on the angles a and b, the y dependencies of the bulk and plume luminescence can have different shapes with respect to one another, as shown. Part (i) of the figure illustrates the case of y = 0.600 in. (The precise details of these shapes depend on the beam spot size and the aluminum hold-down ring diameter.)

geometry studied using 24-eV electrons.<sup>16</sup> These electrons deposit all of their energy within a few monolayers of the surface, yet  $Y_S$  saturates at the very large film thickness of ~ 1000 monolayers.<sup>16</sup>

Figure 8 also shows the  $Y_{L,9.8 \text{ eV}}$  thickness dependence measured using the spectrometer tuned to 9.8 eV. The



FIG. 8. Film thickness dependence of the QMS sputtering yield and the 9.8-eV luminescence yield. The solid curves are fits to a model discussed in Sec. IV.

solid line is again a fit to the model to be discussed in Sec. IV. The yield eventually increases linearly with increase in film thickness, but for films thinner than about 60 monolayers, the luminescence is strongly quenched. As reported earlier,<sup>17</sup> the precise shape of the  $Y_{L,9.8 \text{ eV}}$ thickness dependence was unchanged within the experimental uncertainties as  $S_e$  was varied by a factor of ~9. The  $Y_{L,9.8 \text{ eV}}$  film thickness dependencies observed for argon films grown on polished Si and Ta substrates were similarly offset from true proportionality, with essentially the same asymptotic thickness intercept as displayed for films grown on the gold-beryllium substrate.

The 6.2-eV luminescence band had a similar thickness dependence to that of the 9.8-eV luminescence. The projected asymptotic thickness intercept was approximately equal to that of the 9.8-eV luminescence.

The thickness dependence of the W band is shown in Fig. 9. There is a strong similarity to the sputtering thickness dependence which was simultaneously measured and is also shown. This corroborates the results given in Ref. 16 even though the saturation thickness observed in that work was much larger than that observed in the present work.

### D. Bulk and surface impurity effects

A variety of bulk impurity experiments were performed. Both  $Y_S$  and  $Y_{L,9.8 \text{ eV}}$  were reduced with increasing impurity concentration.  $Y_{L,9.8 \text{ eV}}$  was very strongly quenched by O<sub>2</sub>. The 6.2-eV luminescence feature was strongly enhanced for O<sub>2</sub> concentrations of up to ~0.2%, and the 7.6-eV luminescence was strongly enhanced for N<sub>2</sub> concentration of up to ~0.8%. The two bands are eventually reduced upon incorporation of still higher concentrations of the respective impurities. The residual 6.2- and 7.6-eV luminescence present with no deliberately added impurities probably reflects the incorporation of small impurity concentrations from the



FIG. 9. Film thickness dependence of the 11.2-eV luminescence yield, open circles, and the sputtering yield, solid circles. The solid curve is a fit to a model discussed in Sec. IV.

residual gases in the vacuum system as the argon films are grown. The slower a film was grown, the higher the 6.2-eV luminescence was observed to be in an otherwise pure film. The impurity effects on luminescence observed in this work are qualitatively consistent with results in the literature.<sup>28,29</sup>

The 6.2- and 7.6-eV luminescence bands displayed fluence dependencies that rose from zero or a small value to some maximum. Examples are shown in Fig. 10. On the same scale as this figure, the 9.8-eV luminescence fluence dependence (Fig. 3) rises at essentially zero fluence. The rising part of the fluence dependence for 6.2- and 7.6-eV luminescence bands does not recur if a film is left unbombarded for  $\sim 10$  min. This indicates that a permanent change was produced by the incident ions.

As impurities were incorporated into the films, there was a change in the shape of the thickness dependence of the sputtering yield. As shown in Fig. 11, the thickness at which sputtering saturates is reduced as  $O_2$  is added to the films. The solid lines are fits to the model discussed in Sec. V. A similar but smaller shift occurred for  $N_2$  impurity.

Surface impurity experiments were done by exposing argon films to a few L of  $O_2$ . This resulted in the quenching of the 11.3-eV feature by about a factor of 5, and the quenching of the W band by about a factor of 10 (the remaining 10% may have been background from scattering of the very high intensity 9.8-eV photon flux inside the monochromator). Overcoating argon films of various thicknesses with ~3 L  $O_2$  resulted in an approximately thickness independent reduction of 9.8-eV luminescence, as shown in Fig. 12. The effect is to shift the asymptotic thickness intercept by about a factor of 2 to larger values, as shown by the solid lines which are fits to the model discussed in Sec. V.



FIG. 10. Ion fluence dependence of the 6.2- and 7.6-eV luminescence yields. On this scale the 9.8-eV luminescence rises at essentially zero fluence. The inset shows the ion-induced spectrum in the (5-10)-eV photon energy range.



FIG. 11. Film thickness dependencies of the sputtering yield for different bulk impurity concentrations of  $O_2$ . The solid curves are fits to a model disussed in Sec. V.

A number of transient effects were observed due both to depositing overlayers of  $O_2$ , and to simply letting the film sit unbombarded to collect surface impurities from the residual gases in the vacuum system. With thick deliberately added  $O_2$  overlayers, the initial argon sputtering yield was reduced, perhaps because the argon surface was buried. Eventually, however, the sputtering yield was considerably enhanced before decreasing to its normal value as all the  $O_2$  is sputtered off the surface. The *W* band was initially quenched, but returned to a



FIG. 12. Film thickness dependencies of the 9.8-eV luminescence yield for argon films with clean surfaces and for argon films with  $\sim 3$  monolayers of O<sub>2</sub> on the surface. The solid curves are fits to a model discussed in Sec. IV.

saturated level after an ion dose which was roughly proportional to the amount of  $O_2$  originally deposited. Similar effects were observed by letting the film sit unbombarded. Long waits of 10 to 30 min, during which  $\sim 1$  monolayer of impurity may be deposited, resulted in large initial sputtering spikes and an initially quenched W band. Because of the waiting time dependence of the initial transient behavior, it is tempting to ascribe these transient effects to surface impurities, although the precise character of the observed transients is not quite the same as when  $O_2$  overlayers are deliberately added.

# **IV. EXCITON MODEL OF SPUTTERING**

A. Conversion of electronic energy into atomic motion by dimer decay

# 1. Gas phase

The internuclear potential-energy diagram for Ar pair interactions is an important key to understanding the conversion of electronic potential energy into the kinetic energy of nuclear motion. The fate of ions and excited atoms in the gas phase is intimately connected with the rich overlap between attractive and repulsive internuclear potential surfaces.<sup>13,33</sup> Figure 13, adapted from



FIG. 13. Gas-phase argon internuclear potential-energy diagram, adapted from Ref. 33. On the right-hand side of the figure the solid-state excitonic energy levels are shown for comparison with the gas phase atomic energy levels. VB denotes valence band.

Ref. 33, shows how ground state and various excited and ionized states of argon interact with neighboring ground-state argon atoms. An  $Ar^+$  ion could undergo the following sequence of decay processes:

$$Ar^{+} + Ar + Ar \rightarrow Ar_{2}^{+} + Ar + E_{kin} ,$$

$$Ar_{2}^{+} + e \rightarrow Ar + Ar^{**} + E_{kin} ,$$

$$Ar^{**} + Ar + Ar \rightarrow Ar_{2}^{**} + Ar + E_{kin} ,$$

$$Ar_{2}^{**} \rightarrow Ar + Ar^{*} + E_{kin} ,$$

$$Ar^{*} + Ar + Ar \rightarrow Ar_{2}^{*} + Ar + E_{kin} ,$$

$$Ar_{2}^{*} \rightarrow Ar + Ar + hv + E_{kin} .$$

The last reaction is a radiative decay, since there is no efficient nonradiative pathway from  $Ar_2^*$  to the ground state. The photon emitted is Stokes shifted by ~2 eV from the lowest excited state and therefore is not reabsorbed. In each dimer decay step, two atoms are repelled from one another with about 0.5 eV of kinetic energy. In the creation and eventual vibrational relaxation of dimers via three body collisions, a net kinetic energy of the order of 1 eV is also released. However, the release takes place in small increments equivalent to a few vibrational energy-level spacings.

## 2. Solid phase

The transition from the gas to the solid-state changes the energy levels and dynamic behavior of excited (exciton) and ionized (hole) states. Figure 13 shows how the gas phase atomic energy levels coordinate to the excitonic solid-state energy levels. The excited states are contained in the 2-eV range in the solid instead of the 3-eV range in the gas phase. Separate groups of atomic lines coalesce into two sets of excitonic levels (n = 1, 2, ...) separated by spin-orbit coupling ( $J = \frac{1}{2}, \frac{3}{2}$ ). The excitonic levels at the equilibrium lattice spacing of 3.8 Å are experimentally known from absorption and reflectance spectroscopy.<sup>34</sup>

A qualitative solid-state internuclear potential-energy diagram can be drawn by combining well depths and equilibrium internuclear separations from the gas phase internuclear potential-energy diagram, with solid-state excitonic energy levels. The decay process of excitons in the solid state is expected to be similar to the decay of ion or excited atom energy in the gas phase. The following decay scheme for holes is suggested as typical:

$$Ar^{+} + Ar \rightarrow Ar_{2}^{+}(vib. hot) + phonons ,$$
  

$$Ar_{2}^{+}(vib. hot) + e \rightarrow Ar + Ar^{*} + E_{kin} ,$$
  

$$Ar^{*} (moving) + Ar + Ar \rightarrow Ar_{2}^{*} + Ar + phonons$$
  

$$Ar_{2}^{*} \rightarrow Ar + Ar + E_{kin} + hv .$$

Figure 14 shows the relevant solid-state potential-energy diagram. In constructing this diagram, care has been taken to account for any distortion of the lattice surrounding an excimer. There is reported to be no distortion about the  $Ar_2^+$  ionic excimer,<sup>43</sup> so that the interac-



FIG. 14. Solid-state internuclear potential-energy diagrams of Ar + Ar,  $Ar + Ar^*$ , and  $Ar + Ar^+$ . The means of constructing this diagram is discussed in the text. Solid line, Ref. 35; dashed line, Ref. 36; dash-dot line, Ref. 37; lower set, Ref. 38 ( $\blacksquare$ ); upper set, Ref. 39 ( $\blacksquare$ ); Ref. 40 ( $\bigcirc$ ); Ref. 41 ( $\times$ ); Ref. 42 (+). The dotted line is the suggested potential-energy diagram of  $Ar + Ar^*$  as discussed in the text. Only the solid line, ( $\times$ ), and (+) represent actual data; the rest of the curves are the results of *ab initio* calculations. The long arrows indicate the suggested decay sequence of an ionic exciton  $Ar^+$ . The equilibrium lattice spacing is 3.8 Å.

tion  $Ar + Ar^+$  is shown at the band gap, 14.2 eV (the electron-hole pair energy of solid argon). The vertical compression of the energy levels in going to the solid state makes possible the repulsive recombination of  $Ar_2^+$ with an electron to form Ar and the n = 1 exciton Ar<sup>\*</sup>. Since these separate energetically into an undistorted lattice, the repulsive interaction  $Ar + Ar^*$  is shown at the first exciton level, 12.2 eV. The correct picture for the attractive interaction  $Ar + Ar^*$  is estimated as follows. 9.8-eV luminescence arises from vibrationally relaxed  $Ar_2^*$  (Ref. 12) which has an equilibrium internuclear separation of 2.42 Å.<sup>38</sup> A vertical radiative decay at this separation to the known ground-state repulsive van der Waals potential<sup>35</sup> leads to the release of 1.1 eV of kinetic energy. Thus, of 12.2 eV energy of an n = 1 exciton from which  $Ar_2^*$  arises, a total 9.8 + 1.1 = 10.9 eV is accounted for by radiative and repulsive energy release. The remainder, 1.3 eV, reflects lattice relaxation associated with the excimer  $Ar_2^*$ . Part of this is due to the binding energy of  $Ar_2^*$  which in the gas phase is 0.68 eV;<sup>38</sup> this leaves approximately 0.6 eV which is thought to be stored in the elastic potential energy of a distorted

cavity of Ar atoms surrounding the  $Ar_2^*$ . This bubble arises due to the negative electron affinity of solid argon,<sup>44</sup> by which the Rydberg electron orbiting the dimer ion core slightly repels the surrounding lattice. In effect, the distorted cavity causes the solid-state attractive well of  $Ar_2^*$  to be slightly deeper than it is in the gas phase, as shown by the dotted line in Fig. 14.

The above suggested decay scheme for  $Ar^+$  is shown by the arrows in Fig. 14. (Intermediate states such as Ar\*\* are ignored in this scheme.) This decay scheme reflects the fact that in the solid atoms do not initially have directed kinetic energy. In the solid, the Ar<sub>2</sub><sup>+</sup> dimers form, "cool" (relaxing toward the  $Ar_2^+$  minimum) via multiphoton emission, and recombine with an electron. The Ar\* created in the repulsive recombination of an  $Ar_2^+$  with an electron is physically moving with a kinetic energy of  $\sim 0.5$  eV and therefore it can undergo an immediate three-body collision leaving a self-trapped, immobile Ar<sub>2</sub><sup>\*</sup> excimer which relaxes via multiphoton emission to the bottom of its well. Thus the two repulsive decays, labeled in the above scheme as  $E_{kin}$ , are expected to occur at nearly the same place in the lattice (but delayed in time by the 9.8-eV radiative lifetime). The repulsive recombination of  $Ar_2^+$  with an electron and the repulsive decay of Ar<sub>2</sub><sup>\*</sup> following 9.8-eV luminescence each release about 1.0 eV of kinetic energy as shown in Fig. 14. These kinetic energies are much larger than the surface binding energy of solid argon, 0.06 eV, and therefore if these decays occur near enough to the film surface (the vacuum interface) they can be responsible for the sputtering process.

The quantum efficiency of  $Ar^+$  to produce 9.8-eV luminescence is thought to be high. When (10-30)-keV electrons are incident upon solid argon, 30-50% of the energy lost in the solid is converted into 9.8-eV luminescence.<sup>28</sup> About 80% of all incident electron-induced excitations of any type are ionization events.<sup>45</sup> Using W=23.6 eV as the average energy required to make a hole-electron pair,<sup>46</sup> it would be expected that ~50% of the deposited electron energy would be converted into 9.8-eV luminescence if the quantum efficiency of  $Ar_2^*$ formation from any initial state is one. Therefore in the models to be discussed we assume the quantum efficiency of  $Ar^+$  is unity.

## **B.** Exciton dynamics

# 1. Bulk behavior

Diffusion of  $Ar^+$  holes is a means of propagating large "quanta" of energy over relatively large distances in the lattice, so that energy initially deposited deep within the film can migrate to the vacuum interface where a subsequent decay process could give rise to atomic ejection. Photon excited excitons diffuse 50 to 100 Å over  $\sim 10^{-11}$  s (Ref. 47) before they are self-trapped as dimers  $Ar_2^*$ . Ar<sup>+</sup> can also diffuse by charge exchange before it is self-trapped as  $Ar_2^+$ . Later we estimate the lifetime of a free hole to be  $10^{-11}$  to  $10^{-10}$  s. Since the thermalization time of a hot electron in the conduction band of solid argon is also of the order of  $10^{-11}$  to  $10^{-10}$  s,<sup>48</sup>

hole self-trapping and direct recombination of holes with electrons might be expected to compete. The failure to observe recombination luminescence at 14.2 eV, however, suggests that the dominant fate of  $Ar^+$  holes is self-trapping rather than direct recombination.

#### 2. Interface behavior

The dynamics of neutral excitons at a metal substrate is fairly well understood. When a neutral exciton approaches a metal surface, an Auger-type process can occur in which the excitonic energy is used to eject an electron from the metal. This two-step photoemission process has been studied in solid xenon<sup>49</sup> and krypton.<sup>50</sup> In both cases, the data were best described by a perfectly quenching substrate boundary condition. In the case of krypton, the efficiency of electron ejection was ~0.3 electron per exciton. This qualitatively matched the results of a gas phase experiment in which metastable  ${}^{3}P_{0}$ Kr atoms were scattered from metal surfaces with resultant electron ejection.<sup>5</sup>

The behavior of holes near a metal substrate has not been studied. However, it is known from gas phase scattering of low-energy ( $\sim 100 \text{ eV}$ ) rare-gas ions from metal surfaces that ions are very efficiency neutralized by an Auger or resonance process. Within one monolayer of the surface, transfer rates can be as high as  $10^{14}$  to  $10^{16} \text{ s}^{-1}$  (Ref. 52) comparable to or faster than an estimated charge exchange hopping rate for diffusion of  $10^{14} \text{ s}^{-1}$  and much faster than the  $10^{11} \text{ s}^{-1}$  hole selftrapping rate discussed above.

The properties of excitons at the vacuum interface are not well understood. The photoemission data from xenon<sup>49</sup> were best described by assuming that the outer surface is a perfect exciton trap. However, the photoemission data from krypton<sup>50</sup> were best described by assuming that the surface is a perfect exciton reflector. Also, details of the photoluminescence spectra of raregas solids were best described by assuming perfect exciton reflectivity of the vacuum interface for clean surfaces, and perfect exciton trapping for dirty surfaces.53 Recently the 11.3-eV (W) luminescence band of Ar was reported to be directly related to the outer surface.<sup>16,54</sup> This suggests the possibility that the outer surface is at least partially exciton and hole trapping and that the radiative deexcitation of surface trapped species differs from the deexcitation in the bulk.

# C. Hole diffusion model of $Y_S, Y_L$ thickness dependencies

### 1. Diffusion equation and boundary conditions

The diffusion and self-trapping of holes excited by an ion beam can be modeled based on the above ideas by a diffusion equation:<sup>14,17,32</sup>

$$D_{+}\frac{d^{2}n_{+}}{dx^{2}}-\frac{n_{+}}{\tau_{+}}+I_{0}\alpha_{+}=0,$$

 $n_{+}(x)$  is the hole density radially and temporally averaged over many incident ion tracks,  $D_{+}$  is the diffusion coefficient of holes, and  $\tau_{+}$  is the trapping lifetime of a hole. The source function of holes,  $I_0\alpha_+$ , is a constant since the swift light ions used in these experiments penetrate completely through the film with only a small change in their energy, thus leaving an essentially uniform path of ionization.  $I_0$  is the flux of incident ions, and  $\alpha_+$  is the linear density of ionization events along an ion track. The hole diffusion length is given by  $l_+^2 = D_+ \tau_+$ . This one-dimensional diffusion equation is derived from the three-dimensional time-dependent diffusion equation for a single-ion track by integrating over time and over spatial coordinates perpendicular to the ion track. Deviations from this form are discussed later.

Owing to the uncertainty in how holes behave at the interfaces, general substrate and vacuum interface boundary conditions are used for the above diffusion equation:

$$D_{+}\frac{dn_{+}(0)}{dx} = \Delta_{f}\frac{l_{+}}{\tau_{+}}n_{+}(0) ,$$

$$D_{+} \frac{dn_{+}(d)}{dx} = -\Delta_{b} \frac{l_{+}}{\tau_{+}} n_{+}(d) ,$$

where d is the thickness of the film. The generality of these conditions is reflected in the parameters  $\Delta_f$  and  $\Delta_b$ , which can each range from 0 to  $\infty$ .  $\Delta=0$  corresponds to an interface being a perfect hole reflector, and  $\Delta = \infty$  corresponds to an interface being a perfect trap. The quantities  $\Delta(l_+/\tau_+)$  are the surface recombination velocities at the front and back surfaces.

Since we assume a hole decays at the place where it is self-trapped,  $n_+(x)/\tau_+$  is the average rate of decay of holes in the bulk. The normalized solution to the diffusion equation is

$$\frac{1}{I_0 \alpha_+} \frac{n_+(x)}{\tau_+} = w_1 e^{x/l_+} + w_2 e^{-x/l_+} + 1 , \qquad (4.1)$$

where

$$w_{1} = \frac{\Delta_{f}(-1 + \Delta_{b})e^{-d/l_{+}} - \Delta_{b}(1 + \Delta_{f})}{(1 + \Delta_{b})(1 + \Delta_{f})e^{d/l_{+}} + (1 - \Delta_{f})(-1 + \Delta_{b})e^{-d/l_{+}}} \to 0 \text{ for } d \gg l_{+} ,$$

$$w_{2} = \frac{-\Delta_{f}(1 + \Delta_{b})e^{d/l_{+}} - (1 - \Delta_{f})\Delta_{b}}{(1 + \Delta_{b})(1 + \Delta_{f})e^{d/l_{+}} + (1 - \Delta_{f})(-1 + \Delta_{b})e^{-d/l_{+}}} \to -\frac{\Delta_{f}}{1 + \Delta_{f}} \text{ for } d \gg l_{+}$$

and where the quantity d is the thickness of the film. Figure 15 is a plot of expression (4.1) showing how the values of  $\Delta$  at the interfaces affect the hole density in the bulk near the interfaces and hence rate of hole decay in those regions. For thick films, i.e., with front and back interfaces separated by a distance of at least several diffusion lengths, the bulk hole decay rate near an interface characterized by  $\Delta$  is fractionally lower by an amount  $\Delta/(1+\Delta)$  with respect to the decay rate deep within the film, the deficit being due to surface trapped species.

If there is any tendency for holes to be trapped or quenched at the interfaces, then at the vacuum and metal interfaces, respectively, the net fluxes of holes are

$$\Phi(0) = D_+ \frac{dn_+(0)}{dx}, \quad \Phi(d) = -D_+ \frac{dn_+(d)}{dx}$$

At an interface characterized by  $\Delta$ , the ratio of the interface hole trapping rate to the hole decay rate far from the interfaces is

$$\frac{1/\tau_{\text{surface}}}{1/\tau_{+}} = \frac{l_{+}}{l_{0}} \frac{\Delta}{1+\Delta} , \qquad (4.2)$$

where  $l_0$  is the lattice spacing and  $\tau_{\text{surface}}$  is an effective lifetime of a hole at the interface, taking into account the preferential trapping or quenching there.

# 2. Dependence of $Y_L$ , $Y_S$ on film thickness

There are three types of luminescence yields  $(Y_L)$  which could be caused by hole decay. Assuming unit efficiency for producing a 9.8-eV photon and no absorption losses, luminescence that originates from hole decay in the bulk of the film is given by



FIG. 15. Solutions to the exciton diffusion equation (4.1) with a variety of interface diffusion boundary conditions characterized by different values of  $\Delta_f$  and  $\Delta_b$ . Results for two different film thicknesses are shown.

$$Y_L(\text{bulk}) = \frac{1}{I_0} \sum_{i=1}^{i=N} \frac{n_+(x_i)}{\tau_+} ,$$

where N is the number of monolayers in the film and  $x_i$  is the depth of the *i*th monolayer. For luminescence from holes which are preferentially trapped at the vacuum interface

$$Y_L(\text{surface}) = \frac{1}{I_0} \Phi(0)$$
.

We assume that Auger processes deexcite holes near x = d without luminescence. The corresponding sputtering yield  $(Y_S)$  is calculated based on two repulsive decays of dimers for each  $Ar^+$  created. (We will ignore the contribution to both luminescence and sputtering arising from excitation to states below the ionization limit.) Sputtering due to holes that decay in the bulk and at the surface is calculated as

$$Y_{S}(\text{bulk}) = \frac{1}{I_{0}} \sum_{i=1}^{i=N} \frac{n_{+}(x_{i})}{\tau_{+}} [\Lambda_{+}(x_{i}) + \Lambda_{*}(x_{i})]$$
  
$$Y_{S}(\text{surface}) = \frac{1}{I_{0}} \Phi(0) [\Lambda_{+}(0) + \Lambda_{*}(0)].$$

In these expressions,  $\Lambda_+$   $(x_i)$  is the average number of atoms sputtered from the surface per repulsive recombination event of  $\operatorname{Ar_2}^+$  at depth  $x_i$  and  $\Lambda_*(x_i)$  is the same for repulsive events following radiative decay of  $\operatorname{Ar_2^*}$ . The functions  $\Lambda_+$  and  $\Lambda_*$  reflect that the deeper in the film a dimer decay occurs, the less effective it is at causing ejection of particles, as shown by the classical dynamics simulation of Garrison and Johnson.<sup>55</sup> Because of the Stokes shift such functions are not needed for modeling the 9.8-eV luminescence.

Using (4.1), for films with  $d \gg l_+$  these yields become

$$Y_L(\text{bulk}) = \alpha_+ \left[ d - l_+ \frac{\Delta_f}{1 + \Delta_f} - l_+ \frac{\Delta_b}{1 + \Delta_b} \right], \quad (4.3a)$$

$$Y_L(\text{surface}) = \alpha_+ l_+ \frac{\Delta_f}{1 + \Delta_f} , \qquad (4.3b)$$

$$Y_{S}(\text{bulk}) \approx \alpha_{+} \overline{\Delta x} \left[ \frac{1}{1 + \Delta_{f}} \right],$$
 (4.3c)

$$Y_{S}(\text{surface}) = \alpha_{+}l_{+}\frac{\Delta_{f}}{1+\Delta_{f}}[\Lambda_{+}(0) + \Lambda_{*}(0)]; \qquad (4.3d)$$

in (4.3c),  $\overline{\Delta x}$  is the weighted "sputter depth,"

$$\overline{\Delta x} = \sum_{i=1}^{i=N} [\Lambda_+(x_i) + \Lambda_*(x_i)] l_0 .$$
(4.4)

From the numerical simulations<sup>55</sup> only terms with  $i \le 5$  contribute significantly for energy impulses of the order of 1 eV.

Assuming that the metal substrate is an efficient nonradiative  $[Y_L(\text{substrate})=0]$  hole quenching site,  $\Delta_b = \infty$ , and that the vacuum interface is a perfect hole reflector,  $\Delta_f = 0$ , then  $Y_L(\text{surface})=0$  and  $Y_S(\text{surface})=0$  as well. The only nonzero yields in this case are  $Y_L(\text{bulk})$  and  $Y_S(\text{bulk})$ . From Eq. (4.3a)  $Y_L$  (bulk) increases linearly with increases in film thickness for thick films and has an asymptotic thickness intercept equal to  $l_+$ .  $Y_S$  (bulk), although arising from bulk decays, is negligible except for decays within a few monolayers of the surface, because of  $\Lambda_+(x_i)$  and  $\Lambda_*(x_i)$  (Ref. 55) and therefore it saturates for thick films to the result in Eq. (4.3c).  $Y_S$  (bulk) is reduced to below 90% of its saturated value for film thicknesses less than about  $3l_+$  because of the influence of the substrate interface on hole quenching. This is summarized in Fig. 15. Figure 16 shows model sputtering and bulk 9.8-eV luminescence thickness dependencies for the case  $\Delta_b = \infty$ ,  $\Delta_f = 0$  based on this model.

If there is any tendency for preferential hole trapping at the vacuum interface, so that  $\Delta_f > 0$ , the shape of the  $Y_{S}(\text{bulk})$  thickness dependence is not dramatically altered. Also, the shapes of  $Y_S(\text{bulk})$  and  $Y_S(\text{surface})$  are essentially indistinguishable if  $\Delta_f \leq 10$ . If species preferentially trapped at the surface give rise to luminescence, then there is a surface luminescence term  $Y_L(surface)$  in addition to the bulk luminescence term.  $Y_L(surface)$  has a thickness dependence almost exactly like that of  $Y_{S}(\text{bulk})$  and  $Y_{S}(\text{surface})$ . If trapped species at the surface give rise to the same luminescence as do bulk trapped species, then the asymptotic thickness intercept of the total luminescence thickness dependence is unaltered, but the slope is nonzero for small thicknesses. However, if  $Y_L($ surface) occurs at a different photon energy or if the surface exciton decay is nonradiative, the 9.8-eV luminescence thickness intercept increases, to a

![](_page_11_Figure_20.jpeg)

FIG. 16. Normalized model bulk luminescence and bulk sputtering yield film thickness dependencies assuming a perfect exciton quenching boundary condition at the substrate and a perfect exciton reflecting boundary condition at the surface. The dashed line indicates the asymptotic thickness intercept of the luminescence.

maximum of  $2l_+$ , as  $\Delta_f$  increases. These model thickness dependences are summarized in Fig. 17.

The ratio  $r_{90}$  of the 90% sputtering saturation thickness to the 9.8-eV luminescence asymptotic thickness intercept is sensitive to the parameters  $\Delta_b$  and  $\Delta_f$ , as summarized in Fig. 18. If  $\Delta_f = 0$  and  $\Delta_b = \infty$ , the ratio is  $\sim 3.1$ . For  $\Delta_b \leq 2$ , and  $\Delta_f = 0$  the ratio becomes significantly greater than three. If only bulk luminescence is observed, and if  $\Delta_b \geq 10$ , then the ratio varies from  $\sim 3.1$  to  $\sim 1.5$  as  $\Delta_f$  varies from zero to infinity.

### D. Comparison of data with theory

With the above models the shapes of the thickness dependences of  $Y_S$  and  $Y_{L,9.8 \text{ eV}}$ , shown in Fig. 8, can be fitted. First it is assumed that the metal substrate is a perfect nonradiative hole sink, and that the vacuum interface is a perfect hole reflector:  $\Delta_f = 0$ ,  $\Delta_b = \infty$ . The simplified models of  $Y_S(\text{bulk})$  and  $Y_L(\text{bulk})$ , shown in Fig. 16, fit the observed film thickness dependencies of  $Y_S$  and  $Y_{L,9.8 \text{ eV}}$  quite well, as shown by the solid curves in Fig. 8. The deduced value of  $l_+$  is large, ~60 monolayers or ~230 Å. Luminescence and sputtering data yield essentially the same diffusion length.

The recently observed correlation between the sputtering and the 11.3-eV (W) luminesence band<sup>16</sup> is corroborated by the present work. As shown by the solid curves in Fig. 9, the thickness dependence of the W band is well fitted by the model  $Y_L$ (surface) shown in Fig. 17, but  $\Delta_f > 0$  must be assumed. About the same value of  $l_+$  is extracted, 74 monolayers, which should be compared to  $l_+ = 67$  monolayers deduced from the sputter-

![](_page_12_Figure_8.jpeg)

FIG. 17. Normalized model luminescence yield film thickness dependencies for different diffusion boundary conditions. The details are discussed in the text.

![](_page_12_Figure_10.jpeg)

FIG. 18. Model predictions for the quantity (90%  $Y_S$  saturation thickness)/(9.8-eV  $Y_L$  thickness intercept). For both curves, only the bulk luminescence was included. If  $\Delta_b = \infty$  and  $\Delta_f = 0$ , the ratio approaches the value of ~3.1, indicated by the extra elongated tic mark.

ing thickness dependence simultaneously measured and also shown in Fig. 9.

The two-step dimer decay model can be used to predict the magnitude of the sputtering yield for thick films using Eqs. (4.3c), (4.4), and (4.3d). In each step of the decay, the repulsive recombination of  $Ar_2^+$  and the repulsive radiative decay of  $Ar_2^*$ , ~1.0 eV of kinetic energy is released, or  $\sim 0.5$  eV per atom. The simulation of Garrison and Johnson<sup>55</sup> allows an estimation of the sputtering yields  $\Lambda_{+}(x_{i})$  and  $\Lambda_{*}(x_{i})$ . Their classical dynamics simulation gives the average erosion yield of a single atom impulsively energized at depth  $x_i$ , with a specified initial kinetic energy and a random initial direction. Then the sputter yields for each step of the dimer decay are estimated at twice the simulated value for a single moving atom, calculated for half the kinetic energy input,  $\sim 0.5$  eV. Table I shows the estimated sputter yields  $\Lambda(x_i)$ .

An important correction is made concerning the sputter yield of dimer decay in the first monolayer. In the decay of  $Ar_2^+$  at the surface, there is a chance that the  $Ar^*$  produced is ejected so that  $Ar_2^*$  is never formed, and therefore no second step repulsive radiative decay occurs. This happens in at most 50% of all decays of  $Ar_2^+$  in the first monolayer. Therefore the conservative correction applied to  $\Lambda_*$  in the first monolayer is to divide it by two. (According to the simulation results,<sup>55</sup> no such correction is necessary for decay events occurring in the second or deeper monolayers since it is never the initially energized atom in these deeper layers which is ejected from the surface.) The sputter depth [Eq. (4.4)] is  $\overline{\Delta x} = 4.3l_0$  with the first layer efficiency

TABLE I. Sputtering efficiency of a dimer repulsively decaying in the *i*th monolayer releasing  $\Delta E \approx 1$  eV of kinetic energy. These efficiencies are obtained from the classical dynamics simulation in Ref. 55. The results for  $\sim 1$  eV of kinetic energy were obtained by interpolating between the results for  $\sim 0.6$  and  $\sim 1.4$  eV of total kinetic energy. A correction to the results of the simulation was made because in the simulation the value used for the surface binding energy U was too small. Using the entries in the table, the sputter depth is  $\overline{\Delta x}$  $\approx 0.146(\Delta E - U)/U$ .

Sputtering efficiency (ejected atoms/decay)	
Layer $x_i$	$\Lambda(x_i)$
1	0.6
2	0.9
3	0.6
4	0.15
5	0.03
> 5	0

 $\Lambda_{+}(0) + \Lambda_{*}(0) = 0.9.$ 

For 1.5-MeV He<sup>+</sup>,  $Y_S$  was observed to be 42. The linear density of initially created holes along an ion track is  $\alpha_{+} \approx N_{\text{Ar}}S_{e}/W$  where  $N_{\text{Ar}}$  is the number density of argon atoms. For 1.5-MeV He<sup>+</sup>,  $N_{\text{Ar}}S_{e} = 68$ eV/monolayer and  $N_{\rm Ar}S_e/W \approx 2.9$  excitons/monolayer. With  $\Delta_f = 0$ ,  $Y_S$  is predicted to be only 12. To account for a yield of 42,  $\Delta_f = 0.27$  is required. Adding the contribution to sputtering due to the small number of ioninduced neutral excitons which have been ignored as noted in Sec. IV C 2 above does not change  $\Delta_f$  appreciably. For 1.5-MeV H<sup>+</sup>,  $Y_S$  was observed to be 2.5. For this ion,  $N_{\rm Ar}S_e/W \approx 0.3$  excitons/monolayer, and a value of  $\Delta_f = 0.07$  is required to explain the observed yield. The difference between  $\Delta_f$  obtained from the two different yields arises from the fact that  $Y_S$  is not quite linear in  $S_e$ . However, from these calculations it is clear that  $\Delta_f \ll 1$ , and this corresponds to the surface being dominantly exciton reflecting. With  $\Delta_f \approx 0.1$  and  $l_{+}=60$  monolayers, Eq. (4.2) implies that the surface trapping rate is about 6 times the bulk trapping rate.

Further examination of the shapes of the  $Y_S$  and  $Y_{L,9.8 \text{ eV}}$  thickness dependencies provides additional indications that  $\Delta_f$  is small and  $\Delta_b$  is large. The measured ratio  $r_{90}$  (discussed earlier) is about three, and if  $\Delta_b = \infty$ , the data are best fitted by assuming  $\Delta_f \leq 0.1$ , as seen from Fig. 18. What is more, a small amount of surface  $O_2$  causes  $r_{90}$  to drop by a factor of 2, which is the largest possible reduction assuming  $\Delta_b = \infty$ , Fig. 18. Thus, not only is the clean argon vacuum interface characterized by  $\Delta_f \leq 0.1$ , but also oxygen overlayers cause  $\Delta_f = \infty$  with holes trapped or quenched at the surface not luminescing at 9.8 eV. This result is consistent with published results,<sup>53</sup> and confirms the significance of the asymptotic intercept in the  $Y_{L,9.8 \text{ eV}}$  film thickness dependence.  $r_{90}$  does not strongly depend on  $\Delta_b$  if  $\Delta_h \gtrsim 10$ , implying the substrate hole-quenching rate is at

least 60 times the bulk hole self-trapping rate using Eq. (4.2).

In order to describe the lifetime,  $\tau_+$ , of a free hole, we first consider hole hopping from site to site by charge exchange. After N jumps, the average distance traveled is  $l_{+} = l_0 (N/6)^{1/2}$ . If  $l_{+}$  is the observed hole diffusion length, then  $\tau_+ = N\tau_0 = 6\tau_0(l_+/l_0)^2$  with  $\tau_0$  the exchange time, about  $10^{-14} - 10^{-15}$  s.<sup>56</sup> For  $l_+/l_0 = 60$ ,  $\tau_+ \approx 10^{-10} - 10^{-11}$  s. Alternatively, if the transport is described by phonon interrupted coherent hole movement, the theory for neutral exciton motion in Ref. 57 can be adopted. In this model, hole trapping is an intrinsic property of a perfect argon lattice, and selftrapping eventually occurs after a particularly "violent" collision with a phonon. Before self-trapping, the hole scattering time by phonons is  $\tau_{\text{scat}} = (\hbar/2\pi)(B/F^2)$ , where B is the hole bandwidth and  $F = (E_{LR}E_{ph})^{1/2}$ .  $E_{\rm ph}$  is a typical phonon energy, 0.006 to 0.009 eV,<sup>13</sup> and  $E_{LR}$  is the amount of energy dissipated by lattice relaxation to form  $Ar_2^+$ .  $E_{LR} \approx 1.3$  eV from Fig. 14. Thus  $F \approx 0.1$  eV. With B = 0.5 eV,<sup>58</sup>  $\tau_{scat} \approx 5 \times 10^{-15}$  s, not very different from  $\tau_0$ . Now, the "coherent" velocity (group velocity) is  $v_g \approx B l_0 / \hbar = 3 \times 10^7$  cm/s. Thus the mean free path before randomization by hole-phonon scattering is  $\overline{l} = \tau_{scat} v_g = 15$  Å. Since  $\overline{l} \ll l_+$  the use of a diffusion model is clearly appropriate. Replacing  $au_0$ above by  $\tau_{\text{scat}}$  we obtain  $\tau_{+} = 7 \times 10^{-12}$  s. A plausible range of values for  $\tau_{+}$  is then  $\sim 10^{-11} - 10^{-10}$  s, i.e., comparable to the electron cooling time<sup>48</sup> and also comparable to the measured lifetime of neutral excitons.<sup>4</sup>

We wish to point out that hole and exciton selftrapping may dominantly depend on film quality rather than on interaction with phonons that would be present even in a perfect lattice. This is seen from the fact that the measured diffusion length is not always the same, both within this work and considering the work of others. The diffusion lengths obtained in this work were sometimes as high as 350 Å, but were more commonly  $\sim$ 230 Å when the films were created in a consistent manner as described earlier. Also, Coletti et al.<sup>16</sup> recently obtained a diffusion length of the order of 1000 Å, even though they mainly excited lower-energy neutral excitons which typically have measured diffusion lengths of 50 to 100 Å.<sup>47</sup> There is a high density of vacancies, dislocations, stacking faults and residual impurities in films grown from the vapor phase at low temperatures.<sup>58</sup> The average distance between dislocations in argon films deposited under conditions similar to those of the present work is 30 to 70 Å,  $^{59}$  and it is easy to believe that this distance could fluctuate from run to run and group to group. Also, the results of Coletti et al.<sup>16</sup> were obtained from films deposited at a temperature of  $\sim 27$ K at which annealing may have taken place, and their substrate was made of graphite on which epitaxial growth of the films is possible. Thus the fact that they observed such a large diffusion length may be related to the use of less defective films. Finally, the incident ions used here penetrate the films fully whereas the lowenergy electrons of Coletti et al.<sup>16</sup> do not. Therefore ion bombardment may serve to determine the film quality (by, for instance, inducing defects) with the resultant

values of  $l_+$  found here. Because of the large contribution to sputtering from surface trapping, it is likely that the gradual decrease in yield, described earlier, is related to enhanced bulk trapping, i.e., decreasing  $l_+$  with increasing defect density.

The exciton model discussed above is linear; all sputtering and luminescence features of it are expected to be proportional to the number of holes produced by a single ion. The experimental observations of Fig. 4 nearly bear this out assuming that the number of holes produced by an ion is proportional to  $S_{\rho}$ . Even if  $S_{\rho}$  fails to represent the hole production accurately, the sputtering and luminescence should retain a constant ratio. Again, this is nearly, but not exactly, the case. Detailed consideration has been given to a number of possible sources of the remaining discrepancy: hole-hole interactions, excimer-excimer interactions, charge state equilibrium in the incident ions, and the creation of species other than Ar<sup>\*</sup> and Ar<sup>+</sup>, such as  $Ar^{2+.60}$  None of these provides a convincing explanation for the small experimental nonlinearity and it will not be considered further in this paper.

#### E. Energy conversion at the surface

Overcoating argon films with Ne layers completely quenched the W band but not the bulk 9.8-eV light,<sup>54</sup> showing that the W band is associated with the surface of the films. Here we observed that low levels of  $O_2$  on the surfaces also quenched the W band. The W band at 11.3 eV is similar to luminescence from vibrationally hot  $Ar_2^*$  luminescence seen in the gas phase at 11.4 eV (see Fig. 14),<sup>12</sup> and therefore it was suggested<sup>54</sup> that the W band is due to vibrationally "hot"  $Ar_2^*$  centers whose vibrational relaxation is orders of magnitude slower than it is for  $Ar_2^*$  in the bulk. The Ne overlayer was suggested to quench the W band by enhancing vibrational relaxation of these "hot"  $Ar_2^*$  dimers.<sup>54</sup>

Coletti et al.<sup>16</sup> gave a different interpretation of the W band. They suggested that since the electron orbiting the  $Ar_2^+$  core of an  $Ar_2^*$  center actually repels the surrounding lattice slightly, the  $Ar_2^*$  center may not be able to remain on the surface. During the dimer's attempt to form a cavity on the surface, it is ejected before significant vibrational relaxation has occurred. The maximum potential energy available for cavity ejection is ~0.6 eV, the amount by which the solid phase  $Ar_2^*$  well is deeper than the gas phase  $Ar_2^*$  well assuming that the equilibrium internuclear separation is the same in both cases.

Our model, described above, can also account for the sputtering of dimers  $Ar_2^*$ . The recombination of  $Ar_2^+$  with an electron at the surface results in the production of a fast  $Ar^*$ , and we noted that this species might exit the film with a probability of about one half. It is also possible on exiting for this  $Ar^*$  to carry with it another Ar atom, giving an  $Ar_2^*$  moving away from the surface. In the present work, the observation of a plume of sputtered particles glowing at 11.2 eV confirms that this luminescence at least in part comes from sputtered dimers. The lifetime of the metastable  ${}^{3}\Sigma_{\mu}^{+}$  vibrationally

hot dimer most likely to be responsible for the plume component of the W band is 275 ns.<sup>54</sup> With an observed plume decay length of ~0.04 cm, the ejection kinetic energy of the dimers would be 0.8 eV, comparable to what is available either from the cavity mode of ejection or from repulsive ejection. Further decay of these dimers could lead to the energetic argon atoms observed in time of fight.<sup>61</sup> The observed quenching of the W band by Ne overlayers<sup>54</sup> is therefore due at least in part to the prevention of escape of material from the underlying argon, rather than to the alteration of the vibrational relaxation of surface-trapped species.<sup>54</sup>

Luminescence corresponding to gas-phase atomic levels (not resolved in the present work) has also been observed, and this was interpreted as being due to sputtered Ar\*, within the cavity ejection mechanism,<sup>16</sup> although the direct repulsive ejection associated with  $Ar_2^+$ as described above is much more likely. The cavity ejection mechanism can be incorporated within the dimer decay model of the present work.  $Ar_2^+$  could exist and recombine in the outer monolayer of the film as assumed in our decay scheme, since the orbiting electron responsible for the distortion of the lattice is absent. However, those surface Ar\* that are not ejected from the film could trap to form Ar<sup>\*</sup><sub>2</sub> and be sputtered as whole dimers by the cavity ejection mechanism.<sup>16</sup> This change is taken into account by setting  $\Lambda_{\star}(0)=2$  instead of 0.6 from Table I. Further division of  $\Lambda_*(0)$  by two approximately corrects for the loss of Ar\* in the repulsive recombination of  $Ar_2^+$ . Taking this change into account, a slightly smaller value of  $\Delta_f = 0.12$  accounts for the observed sputtering yield due to 1.5-MeV He<sup>+</sup> ions.

### V. IMPURITY EFFECTS

# A. General model of impurity effects

Since the film thickness dependencies of sputtering and luminescence are predicted to be related to the exciton diffusion length  $l_+$ , the O<sub>2</sub> and N<sub>2</sub> doping experiments discussed in Sec. III D test the possibility that impurities may serve as traps or quenching sites for free excitons. The observed reduction in the sputtering saturation film thickness due to impurities indicates a reduction of  $l_{+}$  according to the exciton sputtering model. Fits [using  $Y_S(bulk)$  in Sec. IV] were made to the thickness dependences of  $Y_S$  in order to obtain  $l_+$  as a function of impurity concentration. The model fits are shown as solid lines through the data in Fig. 11. Figure 19 shows these data expressed in the quantity  $[l_{\perp}/l_{\perp}(\text{pure})]^2$  where  $l_{\perp}(\text{pure})$  is the diffusion length with the lowest impurity concentration achievable by us and  $l_{\perp}$  is the value for films with various added O<sub>2</sub> impurity concentrations. Similar results are obtained using  $N_2$  impurity. Because the changes in  $l_+$  were small they were more difficult to extract from fits to the 9.8-eV luminescence film thickness dependence.

The reduction of  $l_+$  when impurities are added to the films confirms that there are ion-induced species which diffuse in the lattice. A general scheme to explain the

D

![](_page_15_Figure_3.jpeg)

FIG. 19.  $O_2$  impurity concentration dependence of the diffusion length squared and the 9.8-eV luminescence yield. Both quantities are normalized by dividing by the pure film values. The solid curves are fits to a model discussed in Sec. V.

impurity effects is shown in Fig. 20. Impurities affect the hole decay chain in two places: the free-hole  $(Ar^+)$ stage and the immobile excimer  $(Ar_2^*)$  stage. The free hole diffuses in the lattice and "encounters" impurity molecules at which trapping or quenching may occur. This interaction is modeled using a rate constant for the loss term in the diffusion equation for free excitons:

$$+\frac{d^{2}n_{+}}{dx^{2}} - \frac{n_{+}}{\tau_{+}} - k_{+}n_{+}[X] + I_{0}\alpha_{+} = 0.$$
Ar +
Ar +
Ar 2
hv
hv
hv

FIG. 20. Schematic diagram of the suggested scheme for explaining impurity effects on sputtering and 9.8-eV luminescence. The solid lines show the normal exciton decay chain including the emission of a 9.8-eV photon. The dashed lines indicate impurity-related alternate exciton decay pathways. Trapping or quenching of free excitons with rate constant  $k_+$  results in a decrease of the observed diffusion length. Longrange energy transfer from  $Ar_2^*$  to impurities results in strong quenching of the 9.8-eV luminescence yield.

Ar

`Ar

[X] is the impurity concentration and  $k_+$  is the exciton-impurity volume density. Since  $D_+$  depends only on the interaction of an exciton with its ground-state neighbors, it is independent of impurity concentration, and the effective diffusion length is altered by the additional loss term as follows:

$$l_{+}^{2} = D_{+}\tau'_{+}$$
 where  $\frac{1}{\tau'_{+}} = \frac{1}{\tau_{+}}(1 + \tau_{+}k_{+}[X])$ .

Since  $l_{+}^{2}(\text{pure}) = D_{+}\tau_{+}$ ,

$$\left(\frac{l_{+}}{l_{+}(\text{pure})}\right)^{2} = \frac{1}{1+k_{+}\tau_{+}[X]}$$

The solid line in Fig. 19 shows that this functional form adequately describes the concentration dependence observed for  $[l_+/l_+(\text{pure})]^2$ .

The results in Fig. 19 indicate that impurities quench Ar<sup>\*</sup> excimers as well as trapping or quenching free excitons. That is, the number of excimers created in an impure film, normalized to the pure film value, is  $[l_{+}/l_{+}(\text{pure})]^{2}$ . Therefore, if all these excimers gave rise to 9.8-eV luminescence,  $Y_L/Y_L(\text{pure}) = [l_+/$  $l_{+}(\text{pure})]^2$  would be expected. In Fig. 19, it is seen that  $Y_L/Y_L$ (pure) <  $[l_+/l_+(0)]^2$ , indicating impurities must also quench some of the excimers. Since excimers are immobile, the quenching mechanism must involve longrange dipole-dipole energy transfer to the impurity. Assuming there is a critical distance  $R_c$  beyond which long-range energy transfer is unlikely, and below which it is very likely, the fraction of Ar<sup>\*</sup><sub>2</sub> surviving to luminesce at 9.8 eV is related to the probability of having no impurities within a distance  $R_c$ . Thus,

$$\frac{Y_L}{Y_L(\text{pure})} = \left[\frac{l_+}{l_+(\text{pure})}\right]^2 (1 - [X]/[\text{Ar}])^{(4\pi/3)(R_c/l_0)^3}$$

where  $l_0$  is the argon lattice spacing and [AR] is the volume density of Ar atoms. Exciton-impurity interaction rate constants and excimer-impurity critical energy transfer radii were deduced from fits to the data in Fig. 19 and for similar data taken with  $N_2$  impurities. For  $O_2$  impurity,  $R_c = 21$  Å and  $k_+\tau_+ = 7 \times 10^{-21}$  cm<sup>3</sup>. For  $N_2$  impurity,  $R_c = 11$  Å and  $k_+\tau_+ = 3 \times 10^{-21}$  cm<sup>3</sup>. Using the  $\tau_+$  estimated earlier  $10^{-10} - 10^{-11}$  s the  $O_2$  reaction rate is consistent with a reaction probability near unity when Ar<sup>+</sup> and  $O_2$  are neighbors.

In a study of electron-induced sputtering of neon, a reduction in the sputtering yield was observed upon doping the neon films with argon.<sup>15</sup> The present work shows the same effect for doped argon films. The dependence of the sputtering yield on impurity concentration is more difficult to model, since the fate of excitonic energy transferred to the impurity system is not well known. However, a general decrease is predicted by the model since the surface trapping term, which is proportional to  $l_+$ , gives a large contribution to  $Y_S$  in both these experiments and those for Ne.<sup>15,32</sup>

## **B.** Energy transfer routes

Some ideas of the specific events that occur upon energy transfer to the impurity system can be obtained by examining the vacuum ultraviolet luminescence spectrum as a function of impurity type and concentration. An important result is that addition of  $O_2$  to the films causes a strong enhancement of a broad band of light at 6.2 eV, and addition of  $N_2$  causes a strong enhancement of a broad band of light at 7.6 eV. This is consistent with previously published results.<sup>28,29</sup> These broad luminescence bands are reminiscent of 9.8-eV luminescence in that the broadness suggests the radiative decay of an excimer to a repulsive van der Waals ground-state potential. The 6.2-eV light may be due to an ArO<sup>\*</sup> ( $^{5}\Sigma$ ) excimer composed of Ar (<sup>1</sup>S) and O<sup>\*</sup> (<sup>5</sup>S<sup>o</sup>) at ~9 eV above the ground state of O, and 7.6-eV light may be due to an ArN<sup>\*</sup> (<sup>4</sup> $\Sigma$ ) excimer composed of Ar (<sup>1</sup>S) and N<sup>\*</sup> (<sup>4</sup>P) at  $\sim 10$  eV above the ground state of N.<sup>29</sup> The extent of the relaxation of these excimers to their energy minima is likely to be  $\sim 1 \text{ eV}$  as in the Ar\* + Ar case. In both cases, radiative decay occurs to a repulsive van der Waals potential, so that energy transferred to the impurity system would contribute to sputtering. Luminescence from more highly excited excimers than these, which includes cases such as Ar\*O and Ar\*N, would probably not occur owing to a dense collection of repulsive potential states which overlap attractive ones, encouraging nonradiative decay. The Ar-O interaction potentials constructed by Rinehart<sup>63</sup> for matrix isolated oxygen indicate radiative decay of the species  $Ar^+O^-$  to the repulsive ground-state ArO could also give rise to photons with energies near 6.2 eV.

The above species suggested to give rise to observed vacuum ultraviolet luminescence bands require the presence of impurity atoms in excited states in order to be created. In a newly grown argon film, however, only impurity molecules are present. The slow rise in the 6.2and 7.6-eV luminescence with ion fluence (Fig. 10) compared to the promptness of the 9.8-eV fluence dependence suggests that dissociation of the molecules and excitation of the fragment atoms to the states needed to form luminescent excimers take place in two separate steps.

The direct creation of O\* (<sup>5</sup>S<sup>o</sup>) and N\* (<sup>4</sup>P) during dissociation of O<sub>2</sub> and N<sub>2</sub> by a hole seems difficult from an energetics standpoint. Two ways for dissociation to occur are charge exchange followed by dissociation of the impurity molecule upon electron recombination, and formation of trimer complexes  $Ar^+O_2$  and  $Ar^+N_2$  which could also result in molecular fragmentation upon electron recombination. However, in the case of N<sub>2</sub>, the energy of N\* (<sup>4</sup>P) with respect to the ground molecular state N<sub>2</sub> ( $X^1\Sigma_g^+$ ), ~20 eV, considerably exceeds the available electronic energy of  $Ar^+$ , 14.2 eV, before charge transfer or trimer formation. In the case of O<sub>2</sub> the energy of O\* (<sup>5</sup>S<sup>o</sup>) with respect to the ground molecular state O<sub>2</sub> ( $X^3\Sigma_g^-$ ), ~14 eV, is only comparable to the initial energy of  $Ar^+$ . Thus, even if charge transfer and trimerization are possible, there are unlikely to be any repulsive potential surface crossings leading to such energetic states as O<sup>\*</sup> (<sup>5</sup>S<sup>o</sup>) and N<sup>\*</sup> (<sup>4</sup>P) upon electron recombination. Ar<sup>\*</sup><sub>2</sub> also lacks sufficient energy to dissociate O<sub>2</sub> to give O<sup>\*</sup> (<sup>5</sup>S<sup>o</sup>) + O (<sup>3</sup>P), or to dissociate N<sub>2</sub> at all. Therefore, for a film initially containing only N<sub>2</sub> or O<sub>2</sub> molecular impurities, there may be no difficulty in fragmenting the molecules, but the atoms created all have insufficient remaining electronic energy to be able to form the observed vacuum ultraviolet luminescent photons at 6.2 and 7.6 eV.

Once impurity atoms are created, exciting them to the appropriate states may occur efficiently, since  $Ar_2^*$  is near in energy to both the atomic energy levels  $O^*$  ( ${}^5S^\circ$ ) and  $N^*$  ( ${}^4P$ ). Also,  $Ar^+$  could trap as dimers such as  $Ar^+N$  and  $Ar^+O$ , which upon electron recombination could directly form the uv luminescent excimers. A more likely possibility is that O atoms serve as electron trapping sites, so that  $Ar^+O^-$  could be directly formed combining the trapping and electron recombination steps.

The fact that the 7.6-eV fluence dependence is slower than the 6.2-eV fluence dependence is expected from the values of  $k_{+}$  and  $R_{+}$  obtained for O<sub>2</sub> and N<sub>2</sub>, since  $k_{+}$ and  $R_{+}$  are smaller for N<sub>2</sub> than for O<sub>2</sub>. These indicate the energy transfer to the N<sub>2</sub> system is less efficient than to the O<sub>2</sub> system. For instance, we note that Ar<sub>2</sub><sup>\*</sup> can dissociate O<sub>2</sub> but probably not N<sub>2</sub>, as the Ar<sub>2</sub><sup>\*</sup> energy does not reach any repulsive potential surface of N<sub>2</sub>. Thus dissociation of O<sub>2</sub> should occur more rapidly than dissociation of N<sub>2</sub>.

### VI. CONCLUDING REMARKS

The present work describes the electronically induced sputtering of solid argon films. The dominant theme has been that the ejection of particles from the solid is a direct consequence of the nuclear motion that occurs as electronic energy deposited in the lattice relaxes. We calculated the erosional effect of an electronic transition occurring between bound and repulsive potential surfaces, which releases repulsive kinetic energy.<sup>13-15,17-19,32,55,61</sup> In the case of argon, we showed that particle ejection is a consequence of nonradiative transitions in the same decay sequence which gives rise to luminescence. We also discussed the possible ejection due to the lattice distortion energy available upon self-trapping of excitons.<sup>16</sup>

Electronic excitation of alkali halides gives rise to halide ejection based on a process very similar to the model we propose for electronically excited argon. In the case of an alkali halide, particle ejection is caused by the recombination of an F center (an electron trapped at a vacant halogen site) and an H center ( $Cl_2^-$  located in what would normally be a single-halogen site).<sup>64</sup> Electronically this is identical to the recombination of  $Ar_2^+$ , except that F-H center recombination is directly to the ground state. Also, because the alkali lattice is more strongly bound and has two constituents, the subsequent details of ejection differ from the case of argon. Nonetheless the similarities between particle ejection from argon and from alkali halides are striking. To summarize the results, a dominant feature of the sputtering and 9.8-eV luminescence yields is the strong film thickness dependencies they display. These dependencies can be explained by a hole diffusion model in which the metal substrate acts as a perfect hole sink, the vacuum interface is primarily reflecting, hole decay near the surface causes sputtering, and hole decay in the bulk gives rise to 9.8-eV photons which escape from any depth. Both thickness dependencies gave rise to the same value of hole-diffusion length, supporting the idea that a free hole is the precursor to a sequence of events leading both to sputtering and to 9.8-eV luminescence. The derived diffusion length was  $\sim 230$  Å, which is large compared to what is observed for n = 1 neutral excitons, 50 to 100 Å.

The ejection process was modeled after gas-phase dissociative recombination and repulsive radiative decay. Included were two stages of repulsive dimer decay,  $\operatorname{Ar}_{2}^{+} + e \rightarrow \operatorname{Ar}^{*} + \operatorname{Ar} + E_{kin}$ , and  $\operatorname{Ar}_{2}^{*} \rightarrow \operatorname{Ar} + \operatorname{Ar} + E_{kin}$ +hv. Realistic estimates were made of the amount of kinetic energy released in these decays by constructing a simple solid-state internuclear potential-energy diagram. The sputtering efficiency of dimer decay was estimated based on published results of a classical dynamics simulation.<sup>55</sup> The magnitude of the observed sputtering yield is accounted for by assuming that the hole source function is  $\alpha_{+} \approx N_{\rm Ar} S_{e} / W$ , and that the trapping probability at the vacuum interface is larger than the bulk trapping. The decay of holes preferentially trapping at the surface accounted for  $\sim 75\%$  of the observed sputtering yield because the efficiency of ejection of atoms from impulsive energy releases is a maximum at the surface. We find that although the vacuum interface is highly reflecting, surface trapping occurs at a rate 6 times that of bulk hole trapping.

In this work, sputtering and W-band luminescence were observed to have similar thickness dependencies, confirming that both are related to hole decay at or near the surface. The W-band luminescence was observed to be present in a plume of sputtered particles extending to  $\sim 1$  mm in front of the target. Based on this and on the fact that vibrationally hot  $Ar_2^*$  in the gas phase gives rise to a luminescence band very similar to the W band, this

- <sup>1</sup>P. Sigmund, Phys. Rev. 184, 383 (1969).
- <sup>2</sup>P. Sigmund, Phys. Rev. 187, 768 (1969).
- <sup>3</sup>H. H. Andersen and H. L. Bay, in Sputtering by Particle Bombardment I, edited by R. Berisch (Springer, Berlin, 1981), p. 145.
- <sup>4</sup>J. P. Biersack and E. Santner, Nucl. Instrum. Methods 132, 229 (1976).
- <sup>5</sup>W. L. Brown, L. J. Lanzerotti, J. M. Poate, and W. M. Augustyniak, Phys. Rev. Lett. 40, 1027 (1978).
- <sup>6</sup>W. L. Brown et al., Nucl. Instrum. Methods 198, 1 (1982).
- <sup>7</sup>R. E. Johnson and W. L. Brown, Nucl. Instrum. Methods **198**, 103 (1982).
- <sup>8</sup>R. E. Johnson and W. L. Brown, Nucl. Instrum. Methods 209/210, 469 (1983).
- <sup>9</sup>C. T. Reimann et al., Surf. Sci. 147, 227 (1984).
- <sup>10</sup>D. B. Chrisey, J. W. Boring, J. A. Phipps, and R. E. Johnson, Nucl. Instrum. Methods B13, 360 (1986).

luminescence is probably due to sputtered dimers  $Ar_2^*$  (Ref. 16) rather than luminescent centers in the very first monolayer of the film.<sup>54</sup> It seems likely that these gasphase dimers form as  $Ar^*$  from the repulsive recombination of  $Ar_2^+$  leaves the surface and dimerizes with a neighbor, but we cannot rule out the possibility that they are expelled during vibrational relaxation near the surface, as they push neighboring atoms away to form a cavity.

Several qualitative impurity experiments produced results which are easily explained in terms of a holediffusion model. Bulk impurities provide trapping or quenching sites for free holes. An alteration in the  $Y_S$ thickness dependencies was expected and found, confirming the correctness of the model. For O<sub>2</sub> impurity, the  $Ar^+-O_2$  interaction is characterized by  $k_+\tau_+ \sim 7 \times 10^{-21}$  cm<sup>3</sup> and the long-range  $Ar_2^*-O_2$  interaction is characterized by a critical separation radius of  $R_c \sim 21$  Å. For N<sub>2</sub> impurity,  $k_+ \tau_+ \sim 3 \times 10^{-21}$  cm<sup>3</sup> and  $R_c \sim 11$  Å. Surface impurities strongly alter the vacuum interface boundary condition for diffusing holes. Monolayer coverages of  $O_2$  on the surface of an argon film have the effect of causing the surface to become an extremely efficient hole trapping or quenching site. This shifts the 9.8-eV luminescence yield dependence on film thickness in the manner expected in the hole-diffusion model.

Sputtering and 9.8-eV luminescence yields are expected to be proportional to the electronic stopping power,  $S_e$ , since the hole-generation function is expected to be proportional to  $S_e$  and hole diffusion, trapping, recombination, and electronic decay are all thought to be processes involving individual holes. Near linearity was observed over a factor of 13 change in  $S_e$ . The small departures from linearity have not been explained quantitatively.

## ACKNOWLEDGMENTS

Partial support of the work of C.T.R. and R.E.J. under the National Science Foundation, Grant No. DMR 86-00469 is gratefully acknowledged.

- <sup>11</sup>J. Jortner, L. Meyer, S. A. Rice, and E. G. Wilson, J. Chem. Phys. **42**, 4250 (1965).
- <sup>12</sup>I. Ya. Fugol, Adv. Phys. 27, 1 (1978).
- <sup>13</sup>R. E. Johnson and M. Inokuti, Nucl. Instrum. Methods 206, 289 (1983).
- <sup>14</sup>C. Claussen, Ph.D. thesis, Odense Universitet, 1982 (unpublished).
- <sup>15</sup>P. Borgesen, J. Schou, H. Sorensen, and C. Claussen, Appl. Phys. A 29, 57 (1982).
- <sup>16</sup>F. Coletti, J. M. Debever, and G. Zimmerer, J. Phys. (Paris) Lett. **45**, L467 (1984).
- <sup>17</sup>C. T. Reimann, R. E. Johnson, and W. L. Brown, Phys. Rev. Lett. **53**, 600 (1984).
- <sup>18</sup>W. L. Brown, C. T. Reimann, and R. E. Johnson, in *Desorption Induced by Electronic Transitions, DIET II*, edited by W. Brenig and D. Menzel (Springer-Verlag, Berlin, 1985), p. 199.

1473

- <sup>19</sup>C. T. Reimann, R. E. Johnson, and W. L. Brown, in Photon Emission from Irradiated Solids, proceedings of the Werner Brandt Workshop on Penetration Phenomena, Oak Ridge, Tennessee, edited by R. H. Ritchie (Oak Ridge Report CONF-850484, 1986), p. 109.
- <sup>20</sup>F. Besenbacher *et al.*, Nucl. Instrum. Methods **191**, 221 (1981).
- <sup>21</sup>W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).
- <sup>22</sup>J. Bottiger et al., Radiat. Eff. 49, 119 (1980).
- <sup>23</sup>J. F. Ziegler, Helium Stopping Powers and Ranges in All Elemental Matter (Pergamon, New York, 1977).
- <sup>24</sup>H. H. Andersen and J. F. Ziegler, Hydrogen Stopping Powers and Ranges in All Elemental Matter (Pergamon, New York, 1977).
- <sup>25</sup>W. L. Brown et al., Nucl. Instrum. Methods 170, 321 (1980).
- <sup>26</sup>W. L. Brown and R. E. Johnson, Nucl. Instrum. Methods B13, 295 (1986).
- <sup>27</sup>F. Coletti and A. M. Bonnot, Chem. Phys. Lett. 55, 92 (1978).
- <sup>28</sup>E. E. Huber, D. A. Emmons, and R. M. Lerner, Opt. Commun. **11**, 155 (1974).
- <sup>29</sup>Yu. B. Poltoratskii and I. Ya. Fugol, Fiz. Nizk. Temp. 4, 783 (1978) [Sov. J. Low Temp. Phys. 4, 373 (1978)].
- <sup>30</sup>A. Hitachi et al., Nucl. Instrum. Methods **196**, 97 (1982).
- <sup>31</sup>R. W. Ollerhead et al., Radiat. Eff. 49, 203 (1980).
- <sup>32</sup>J. Schou, P. Borgesen, O. Ellegaard, H. Sørensen, and C. Claussen, Phys. Rev. B 34, 93 (1986); O. Ellegaard, J. Schou, and H. Sørensen, Nucl. Instrum. Methods B13, 567 (1986).
- <sup>33</sup>D. C. Lorents, Physica **82C**, 19 (1976).
- <sup>34</sup>R. Haensel et al., Phys. Rev. Lett. 23, 1160 (1969).
- <sup>35</sup>R. A. Aziz and H. H. Chen, J. Chem. Phys. 67, 5719 (1977).
- <sup>36</sup>H.-J. Böhm and R. Ahlichs, J. Chem. Phys. 77, 2028 (1982).
- <sup>37</sup>W. R. Wadt, J. Chem. Phys. 68, 402 (1978).
- <sup>38</sup>R. P. Saxon and B. Liu, J. Chem. Phys. **64**, 3291 (1976).
- <sup>39</sup>T. L. Gilbert and A. C. Wahl, J. Chem. Phys. 55, 5247 (1971).
- <sup>40</sup>F. Spiegelmann and J.-P. Malrieu, Chem. Phys. Lett. 57, 214 (1978).
- <sup>41</sup>D. C. Lorents, R. E. Olsen, and G. M. Conklin, Chem. Phys. Lett. **20**, 589 (1973).

- <sup>42</sup>K. T. Gillen et al., J. Chem. Phys. 64, 1925 (1976).
- <sup>43</sup>S. D. Druger and R. S. Knox, J. Chem. Phys. 50, 3143 (1969).
- 44Z. Ophir et al., J. Chem. Phys. 69, 650 (1975).
- <sup>45</sup>T. Doke et al., Nucl. Instrum. Methods 134, 353 (1976).
- <sup>46</sup>M. Miyajima et al., Phys. Rev. A 9, 1438 (1974).
- <sup>47</sup>N. Schwentner, E.-E. Koch, and J. Jortner, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, in press), Vol. III.
- <sup>48</sup>U. Sowada, J. M. Warman, and M. P. De Haas, Phys. Rev. B 25, 3434 (1982).
- <sup>49</sup>Z. Ophir et al., J. Chem. Phys. 63, 1072 (1975).
- <sup>50</sup>N. Schwentner, G. Martens, and H. W. Rudolf, Phys. Status Solidi B 106, 183 (1981).
- <sup>51</sup>F. B. Dunning, R. B. Rundel, and R. E Stebbing, Rev. Sci. Instrum. 46, 697 (1975).
- <sup>52</sup>H. Hagstrum, Phys. Rev. 96, 336 (1954).
- <sup>53</sup>Ch. Ackerman et al., J. Lumin. 12/13, 315 (1976).
- <sup>54</sup>E. Roick et al., J. Phys. C 17, 945 (1984).
- <sup>55</sup>B. J. Garrison and R. E. Johnson, Surf. Sci. 148, 388 (1984).
- <sup>56</sup>R. E. Johnson, J. Phys. B 3, 539 (1970).
- <sup>57</sup>Y. Toyozawa, VUV Radiation Physics, edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon, New York, 1974), p. 317.
- <sup>58</sup>Rare Gas Solids, edited by M. L. Klein and J. A. Venables (Academic, New York, 1977), Vols. I and II.
- <sup>59</sup>S. I. Kovalenko and N. N. Bagrov, Fiz. Tverd. Tela (Leningrad) **11**, 2724 (1969) [Sov. Phys.—Solid State **11**, 2207 (1970)].
- <sup>60</sup>C. T. Reimann, Ph.D. thesis, University of Virginia, Charlottesville, 1986 (unpublished).
- <sup>61</sup>R. Pedrys, D. J. Oostra, and A. E. de Vries, in *Desorption In*duced by Electronic Transitions, DIET II, edited by W. Brenig and D. Menzel (Springer, Berlin, 1985), p. 190.
- <sup>62</sup>Th. Förester, Ann. Phys. (N.Y.) 2, 55 (1948); D. L. Dexter, J. Chem. Phys. 21, 836 (1953).
- <sup>63</sup>T. A. Rinehart, Ph.D. thesis, University of Rochester, 1981 (unpublished).
- <sup>64</sup>P. D. Townsend and F. Lama, in *Desorption Induced by Electronic Transitions, DIET I*, edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer, Berlin, 1983), p. 220.