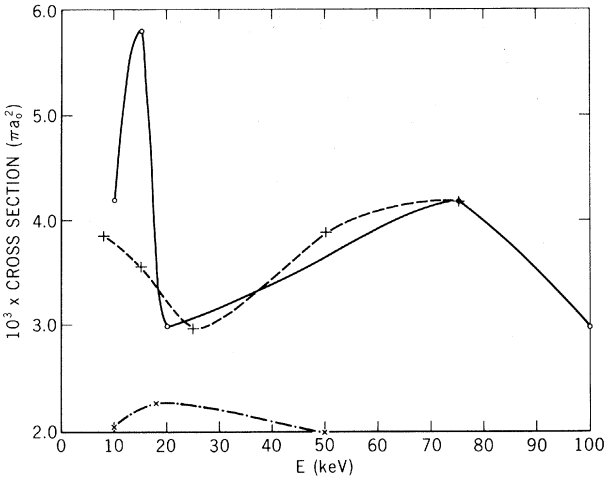

FIG. 1. Solid curve, 1^1S-3^1D experimental excitation cross section estimated from the curve in Ref. 8; dashed-dotted curve, cross section for capture into the $3d$ state of H estimated from the curve in Ref. 9; dashed curve, theoretical excitation cross section based on Eq. (7).

capture cross sections on the average are predicted to be equal to each other with a magnitude σ_F. The minimum in the van den Bos 3^1D excitation function is of magnitude 2.64×10^{-19} cm^2 at 20 keV; the single maximum in the $3d$ capture cross section of Hughes *et al.*[9] is of magnitude 2.0×10^{-19} cm^2 at about 18 keV, in general agreement with the theoretical predictions (see Fig. 1). Unfortunately the van den Bos 3^1P curve does not show the same well-resolved structure; however, the capture peak of Hughes *et al.*[9] correctly occurs at the shoulder of the van den Bos curve.

We take Eq. (6) to be of the form (v is the incident velocity)

$$Q^{ex}=\sigma_F-\alpha(v^{1/2})\cos(\pi\beta v^{-1}-\tfrac{1}{4}\pi) \quad (7)$$

and choose the parameters by normalizing to the van den Bos 3^1D cross section at its second maximum at about 75 keV. Figure 1 shows this result along with the peak of the $3d$ capture cross section. Note that the frequency and phase of oscillation appear to agree fairly well with experiment above 20 keV but that the $v^{1/2}$ dependence for the amplitude is incorrect and the wavelength does not decrease fast enough with increasing v^{-1}. It is hoped that further refinements in the theory and further experiments will elucidate this structure in greater detail.

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Optical Radiation from Low-Energy Ion-Surface Collisions

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Low-energy ion-surface collisions have been observed to result in the emission of optical radiation arising from sputtering with simultaneous excitation. Emission functions have been obtained showing structure and energy thresholds which provide detailed information important in the understanding of this newly observed low-energy phenomenon. These data can be understood in terms of excited-state sputtering efficiencies and radiationless de-excitation processes which compete with radiative de-excitation of the excited states of the sputtered atoms.

We have observed the production of optical radiation due to sputtering with simultaneous excitation when low-energy ions (10 to 3000 eV) impact on surfaces. These are the first measurements of optical radiation arising from excited sputtered surface atoms or molecules produced by low-energy ion-surface collisions. In addition, relative emission functions (photons

detected per incident ion) have been obtained as a function of ion energy for prominent optical lines. In some cases these emission functions exhibit unexpected energy thresholds and structure similar to that seen in the emission cross sections for optical lines produced in low-energy ion-atom collisions.[1,2] Previous studies of optical excitation by ion-surface impact have been performed at much higher energies and have not revealed the structure at the lower energies.[3-6] In most cases at the low ion-impact energies used in this study there is no sharp energy threshold exhibited in the emission function, only a monotonic rise with increasing energy. For these cases, the shapes of the emission functions are in qualitative agreement with a model which assumes radiationless de-excitation processes, Auger de-excitation, or resonance ionization, in competition with the observed radiative de-excitation of the excited states. In addition to their intrinsic interest, these results may have important bearing on plasma, solid state, and space-physics phenomena.

The apparatus for these experiments consisted of an electron-bombardment ion source, electrostatic focusing lenses, and a target chamber. The pressure in the target chamber was $\sim 5\times 10^{-7}$ Torr with 10^{-3} Torr in the source chamber. The normal to the target surface was oriented at an angle of ~45 deg with respect to the incident ion-beam direction. Radiation from the ion-surface collisions was detected by using single-photon counting techniques with a 0.3-m, $f/5$ McPherson monochromator, and a cooled model S-20 photomultiplier. Ion-beam current varied as a function of energy from $\sim 1\times 10^{-7}$ A at 10 eV to $\sim 1\times 10^{-5}$ A at 3 keV. The surface target materials used in these studies include Cu, Ni, Si, C, and Ge; ion beams used were H_2^+, He^+, Ne^+, N_2^+, and Ar^+.

The radiation that we have observed when low-energy ions impact on a surface consists of lines from low-lying excited states of the neutral sputtered surface material, and lines and bands that are characteristic of surface contaminants. Contaminants identified include hydrocarbons (from CH radiation at ~3900 and ~4300 Å), strontium (from radiation at 4607, 4215, and 4078 Å arising from a strontium-impregnated nickel surface), and sodium (from radiation at 5890 and 5896 Å). All ion species used were observed to sputter surface material in excited states, but the excited-state sputtering efficiencies of H_2^+ and He^+ are $\leq 10\%$ of that of Ne^+, N_2^+, and Ar^+ at constant energy. In addition, very intense Balmer lines of neutral hydrogen are observed in H_2^+ bombardment. We ascribe this radiation to collisions of H_2^+ with hydrogen absorbed on or imbedded in the surface in contrast to previous experiments[7-9] in which neutral-hydrogen radiation was attributed to impact neutralization and excitation of the incident ion. Heating the target produces a drastic reduction in the neutral-hydrogen signal while the radiation that is characteristic of sputtered-surface target material is not significantly affected by the increase in temperature. In these experiments, we have shown that the radiation arises from sputtered target atoms or contaminant atoms which leave the surface in excited states, in contrast to the glow discharge phenomena where sputtered ground-state atoms are excited by electron collisions in the plasma surrounding the cathode.[10,11]

Figure 1 shows the measured relative emission functions (photons detected per incident ion) for a number of the spectral lines characteristic of sputtered surface target atoms and one contaminant atom (strontium on a nickel surface at 4607 Å) that are created in excited states. The general trend in the emission function is that of a completely undefined threshold and a gradual rise with increasing energy. Exceptions are noted in the emission functions of N_2^+ on Ni (Ni I, 3369 and 3374 Å) and N_2^+ on Cu (Cu I, 3247 Å) which show conspicuous structure.

The absence of a well-defined threshold and the general shape of the emission functions of most of the spectral lines can be qualitatively understood if it is assumed that radiationless de-excitation processes, perhaps resonance ionization or Auger de-excitation, compete with the radiative de-excitation of the excited states of the sputtered atoms. Evidence for radiationless de-excitation processes has been observed in ion-surface collision experiments at much higher energies (80 keV).[6] The transition rate, $P(s)$, as a function of distance, s, from the surface for either the Auger process or resonance ionization has been approximated by[12,13]

$$P(s) = Ae^{-as}, \tag{1}$$

where A is the radiationless transition rate at the surface. The probability, R, that a sputtered atom in an excited state can escape (to "infinity") without undergoing radiationless de-excitation is then given by[6]

$$R = e^{-A/av_\perp}, \tag{2}$$

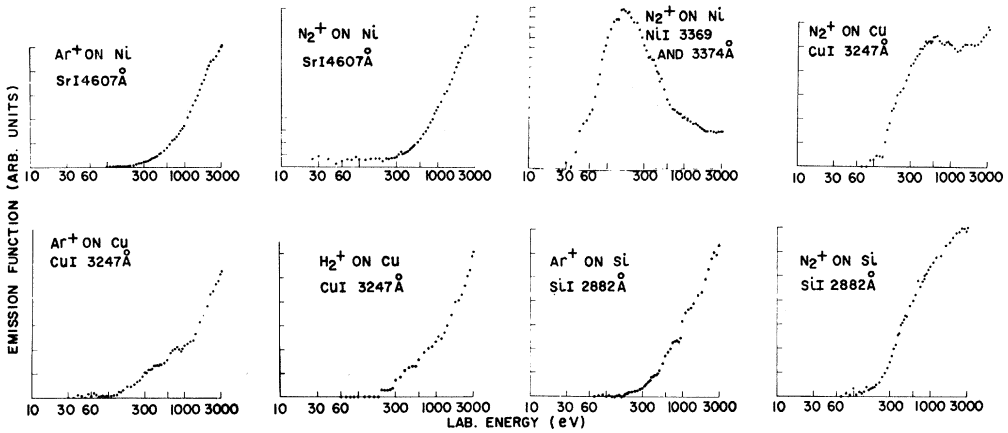

FIG. 1. Emission functions for optical lines produced in ion-surface collisions. The collision combination and an observed line are indicated with each emission function. In two of the graphs the observed radiation at 4607 Å arises from excited strontium atoms which are sputtered from a strontium-impregnated nickel surface. Each graph is plotted independently in arbitrary units.

where $v_\perp$ is the velocity component of the sputtered atom normal to the surface. Thus the probability of escape from the surface in an excited state increases exponentially as the velocity increases so that only the fast excited sputtered neutrals are expected to contribute substantially to the observed signal.[13]

Taking into account radiationless de-excitation processes, the emission function can be approximated by

$$F(E_0) = k\eta(E_0)\int_0^{v_{\max}(E_0)} f(v_\perp)R(v_\perp)dv_\perp, \qquad (3)$$

where k is a constant dependent on geometry but independent of ion energy, $\eta(E_0)$ is the excited-state excitation efficiency defined as the number of sputtered atoms created in a given excited state per incident ion, $f(v_\perp)$ is the perpendicular velocity distribution of the sputtered excited atoms, and R is the survival probability as defined above. An exact form for $f(v_\perp)$ is not available; however, we assume that sputtered excited neutrals have the same perpendicular velocity distribution as measured for the total of all excited and ground-state sputtered neutrals of a given species. Consequently we approximate $f(v_\perp)$ by $e^{-cv_\perp}$, where c is a constant. In the case of Ar^+ on Cu, we may obtain a value for c from the measurements of Stuart, Wehner, and Anderson[14] to be $c \sim 2.5\times10^{-6}$ sec/cm. In the expression for the survival probability, a value $A/a = 2\times10^6$ cm/sec was obtained by Van der Weg and Bierman[6] who studied the Doppler-broadened line profile of CuI 3247 Å observed in the impact of Ar^+ (at 80 keV) on Cu.

The upper limit of integration $v_{\max}(E_0)$ is defined as the maximum perpendicular velocity component of the sputtered atoms. An expression for this quantity can be derived by considering the maximum energy which can be transferred from a projectile ion of mass m_1 and energy E_0 to a surface atom of mass m_2 assuming elastic biparticle collisions. For the geometry used in this experiment (ion beam direction at 45 deg with respect to the surface normal), the maximum perpendicular component of velocity $v_{\max}$ can be shown to be

$$v_{\max} = 1.46\times10^{-1}\left[\frac{4m_1m_2}{(m_1+m_2)^2}\right]^{1/2}\left(\frac{2E_0}{m_2}\right)^{1/2}. \qquad (4)$$

Using the above expression for $v_{\max}$, assuming a constant value for $\eta(E_0)$, and using the value for c previously mentioned, the emission function $F(E_0)$ for Ar^+ on Cu has been calculated for various values of A/a. The calculated values are shown, along with the measured emission function, all normalized to unity at 3000 eV, in Fig. 2(a). The best fit at intermediate and higher energies is for $A/a = 2\times10^6$ cm/sec. Our value for A/a derived from the emission function for CuI 3247 Å in the case of Ar^+ on Cu agrees very well with the value (also 2×10^6 cm/sec) obtained by Van der Weg and Bierman[6] at much higher energies. This agreement is gratifying considering the simple assumptions used in our calculation and the difference in energy range of the two experiments, and it suggests that in our experiment the fast excited neutrals which contribute most to the observed radiation arise from one or a series of nearly elastic biparticle collisions.[15,16]

A probable reason for the discrepancy between

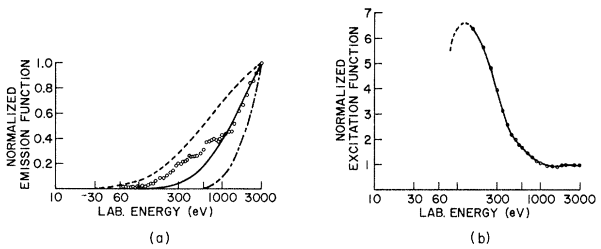

FIG. 2. (a) Comparison of three calculated emission functions computed using A/a values of 7.5×10^5 cm/sec (dashed line), 2×10^6 cm/sec (solid line), and 5×10^6 cm/sec (dot-dashed line) with the measured emission function (open circles) for Cu I 3247 Å in the case of Ar^+ on Cu. (b) Postulated relative excitation efficiency (number of sputtered atoms created in a given excited state per incident ion) which produces agreement between calculated and measured emission functions as shown in (a) at low energies for a value of A/a of 2×10^6 cm/sec. The dashed line represents the expected low energy behavior.

the measured and calculated emission function in the low-energy region is the existence of a nonuniform, excited-state excitation efficiency. Of course in the very low-energy region where the inelastic energy transfer becomes comparable to the maximum value for possible elastic energy transfer, the assumption of elastic collisions is no longer valid. If we assume that the deviation of the measured function from the calculated function is due primarily to a variation in the excited-state excitation efficiency, then the excitation efficiency which is required to force agreement with the measured emission function in the range 150 to 3000 eV can be obtained and is shown in Fig. 2(b) (normalized to unity at 3000 eV). This derived excited state excitation efficiency has a peak at low energies and is relatively flat from 800 eV to 3 keV. This type of behavior has been observed in ion-atom excitation experiments.[17] The excitation efficiency must go to zero as the energy decreases toward threshold, and this expected behavior is indicated by the dashed line in Fig. 2(b).

These studies demonstrate that excited atomic and molecular states play an important role in low-energy sputtering processes. Any future theoretical description of sputtering in the low-energy region must take into account atomic excitation processes at surfaces due to ion impact. Emission functions and excitation thresholds will provide important data for these calculations and to the extent that these excitation processes can be described by one or a series of simple collisions,[16] comparison can be made with appropriate ion-atom excitation measurements. In addition, the technique of observing radiation produced in low-energy ion-surface collisions should find wide application both in the study of radiationless de-excitation processes and in the identification of the constituents of a surface of unknown composition in a relatively nondestructive manner.

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