Effects of Weak External Electric Fields on Photon and Particle Emission from Ion Bombarded Solid Argon

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We have observed that a weak applied external electric field dramatically affects the secondary electron emission, luminescence, and electronic sputtering from thin Ar films bombarded by MeV H^+, He^+, and Ne^+. For MeV H^+ and an external field of only 70 V/cm, the electron yield is equal to the number of electron-hole pairs created, the luminescence from the electron-hole recombinations is eliminated, and the sputtering is reduced by 45%. These effects decrease for heavier projectiles. For the first time, the relative contributions of ionizations and excitations to sputtering can be separated.

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Ionization is an important phenomenon in insulators like electronic materials and biological systems subject to ionizing radiation or high electric fields. The rare gas solids are useful model systems for studying these effects because their electron states are well known, and because aspects of these monatomic van der Waals solids can be treated as dense gases with generally negligible chemical changes [1–3].

When solid Ar is exposed to MeV particles, electronic energy is deposited in the form of ionization (electron-hole pairs) and direct excitation (excitons). These give rise to luminescence and sputtering (desorption). The sequence of events is described by the following well-known model [4,5]. The atomic holes and excitons diffuse primarily by resonant processes. A hole can strongly attract a ground state atom, trap by interacting with lattice vibrations, and form the Ar_2^+ dimer hole in $\sim 10^{-11}$ s. Recombination of the Ar_2^+ with a thermalized electron produces Ar^*, a ground state Ar atom, and kinetic energy; if this recombination occurs near the surface, it can produce sputtering of the Ar or Ar^* involved, or even of neighboring atoms struck by the separating pair. Ar^* can also be produced directly by the projectile or by its associated electronic collision cascade. Regardless of how an Ar^* is formed, it can pair with a neighboring ground state atom in an attractive or repulsive state. If it is in the repulsive state and is at the surface, it can desorb by cavity ejection [6]. If it is in the attractive state, it can combine with an Ar and form the Ar_2^* excimer by interacting with lattice vibrations. The Ar_2^* excimer will decay by emission of a 9.8 eV photon to the repulsive part of the ground state of Ar_2 in $\sim 10^{-9}$ s. The kinetic energy released in this decay is again responsible for sputtering if the decay occurs close to the surface.

Several studies of solid argon have shown the correlation between luminescence and sputtering with electronic stopping power of the projectile [5–9]. In other experiments on the luminescence and charge collection in liquid Ar bombarded by fast particles [10–12], it has been found that charge separation reduces luminescence by eliminating electron-hole recombination. There are, however, still significant gaps in our knowledge of how the behavior of the electrons and holes affects both luminescence and sputtering. We have thus measured *simultaneously* per incident ion the electron yield γ (the number of electrons emitted into vacuum), the 9.8 eV bulk excimer luminescence yield L (light intensity), and the sputtering yield Y (the number of Ar atoms removed) from solid Ar under MeV ion bombardment. By measuring the dependence of these quantities on an applied external electric field, type of projectile, and projectile energy, we demonstrate that hole trapping precedes desorption, and we separate for the first time the contributions of ionizations and direct excitations to sputtering. We find that a weak applied external field has surprisingly profound effects on the luminescence and sputtering, and that these effects depend dramatically on the ionization density in the track of an ion.

The experiments were done in an ultrahigh vacuum chamber ($\sim 1 \times 10^{-10}$ Torr at the target) using H^+, He^+, and Ne^+ in the 0.7–3.0 MeV range, typically at beam current densities of $(2-4) \times 10^{11}$ ions/cm^2 s. Argon films were grown on a gold coated Si wafer at 8 K, by vapor deposition of 99.9999% pure Ar. At the beginning of each run and every 4 h thereafter, the target temperature was raised to 200 K and a 100 Å layer of gold was evaporated onto the substrate. A clean substrate and pure Ar are essential for reproducibility in these experiments. Figure 1 shows the experimental setup. There are two concentric liquid-N_2–cooled copper cylinders surrounding the target; the inner one is an anode for collecting electrons from the bombarded film and is 4.3 cm from the beam spot on the target. An ultraviolet spectrometer detects the 9.8 eV photons emitted from the Ar films, and a quadrupole mass spectrometer calibrated

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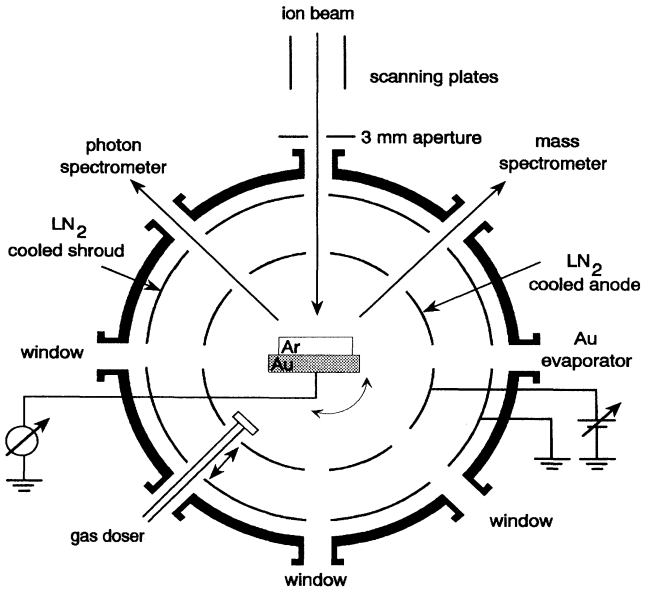

FIG. 1. Experimental setup.

with Rutherford backscattering measures sputtering. In Fig. 2 is an example of the data for the case of 2 MeV H^+ incident on a 750 Å Ar film. The positive voltage on the anode is scanned up to saturation and back down (in ~45 s) while measuring γ, L, and Y. The arrows indicate the direction of the bias scan; the hysteresis will be discussed below.

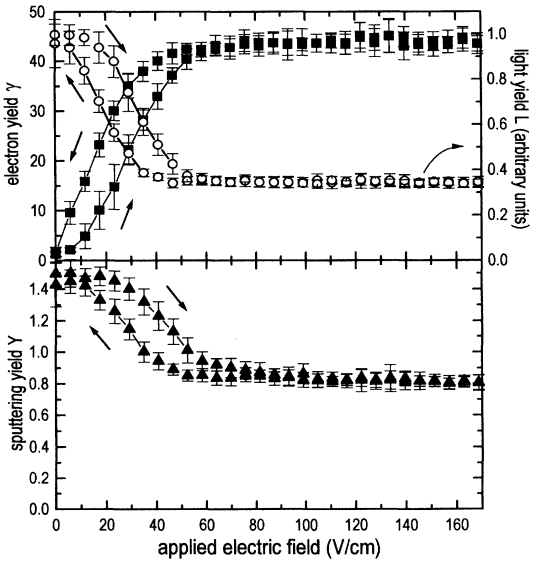

FIG. 2. Electron yield γ, luminescence yield L, and sputtering yield Y as a function of applied electric field for 2 MeV H^+ on 750 Å Ar film.

Figure 3 shows the ratios γ^S/ν, L^S/L^0, and Y^S/Y^0 as a function of the stopping cross section S_e, where the superscripts S and 0 indicate saturation and zero electric field, respectively, and where ν is the number of electron-hole pairs produced in the film by the projectile. The value of ν is given by $\nu = \Delta E/W$, where ΔE is the electronic energy deposited in the film, and $W = 27$ eV is the mean energy spent to create an electron-hole pair [1] at these projectile energies. These ratios in Fig. 3 are plotted to show more clearly how the effect of the applied external electric field depends on ionization density.

The *electron* yield produced by 2 MeV H^+ saturates to values very close to the expected total number of ionizations, i.e., $\gamma^S/\nu = 1$. For example, for 750 Å films and 2 MeV H^+, we calculate $\Delta E = 1.2$ keV [13] and $\nu = 45$, close to the measured $\gamma^S = 45 \pm 1$. As the ionization density (S_e) increases, however, γ^S/ν decreases; for 3 MeV Ne^+ only one-quarter of the electrons produced are collected. The electron yields from solid Ar are not only orders of magnitude larger than those seen from metals but also larger than those seen from other insulators [14]. This can be understood by noting two properties of solid Ar: a large electron escape depth (~5000 Å [15]) and a negative electron affinity (−0.3 eV [1]). This means that the solid can lose even thermalized conduction electrons from large depths. We note that the electrons are overwhelmingly from the Ar and not from the substrate because the measured electron yield for 2 MeV protons from gold into vacuum is only 0.40 electron/ion, and the photoelectron yield of 9.8 eV photons from gold is only 0.03 electron/photon [16], or <1 electron/ion for this case.

The *luminescence* yield at zero external field, L^0, is directly proportional to S_e over the measured range, as

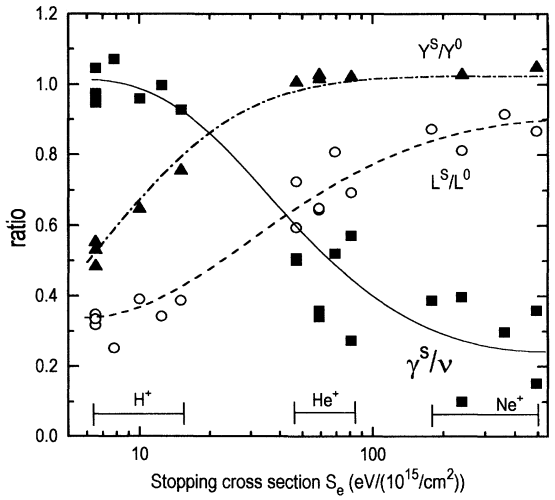

FIG. 3. Fractions of γ/ν, L^S/L^0, and Y^S/Y^0 as a function of stopping cross section [13] for 750–1000 Å thick Ar films. The lines are to guide the eye.

observed before for $S_e < (100\ \text{eV})/(10^{15}/\text{cm}^2)$ [5]. The decrease of L by a weak external field (Fig. 3) is greatest (65%) for low S_e projectiles (2 MeV H^+), and least (10%) for high S_e projectiles (3 MeV Ne^+). This increase of L^S/L^0 and the concomitant decrease of γ^S/ν with S_e indicate the following. For low S_e, the applied field is able to produce complete charge separation, extracting the electrons, and forcing the holes to the substrate, where they recombine nonradiatively [17], thus reducing L. The luminescence, however, is not completely eliminated when we get complete charge separation; we attribute this residual luminescence to excimers resulting from direct excitations to excitonic states (i.e., not from electron-hole recombinations). The fraction of direct excitations (35%) agrees with that observed (33%) for ^{207}Bi conversion electrons in liquid Ar [11]. Unlike the case of low ionization densities, for high S_e, the space charge of the ion track is too great for the electrons and holes to be separated quickly by the electric field, allowing electrons and holes to recombine.

The *sputtering* yield at zero external field is also directly proportional to S_e over the measured range. Figure 3 shows that Y^S/Y^0 also increases with increasing S_e (as did L^S/L^0), but has a higher value at low S_e of 55%. This is the first report of a dependence of sputtering on external electric fields. We expect Y^S/Y^0 to behave similarly to L^S/L^0 because sputtering mainly results from the kinetic energy of repulsion occurring after the 9.8 eV luminescence decay. The higher value of Y^S/Y^0 at low S_e and the different initial dependence of Y^S/Y^0 on increasing S_e from that of L^S/L^0 indicate that there is an additional sputtering process that occurs before trapping. This may be due to the repulsive ionic states [18,19] resulting from Ar^{2+} decay. Our results are consistent with the observation of sputtering without luminescence for very thin Ar films (<200 Å) [5]. Now we can assign a lower bound of 45% of total sputtering to processes starting from ionization events.

The following picture accounts for the above observations. When the projectile passes through the Ar film, it forms a "plasma" of electron-hole pairs. The external electric field begins to extract electrons, eroding the plasma, similar to what happens in a solid state nuclear particle detector. The unbalanced positive charge induces a larger field inside the film, driving the holes quickly toward the substrate. This process continues until all the holes are quenched at the substrate and all the electrons are extracted, or until the holes begin to trap and recombine with electrons. For low S_e, we are able to efficiently move the holes to the substrate to recombine nonradiatively. For high S_e, the applied field cannot overcome the space charge of the track to remove the holes before they are able to recombine.

The field induced in the film can be approximated with a simple model. For a hole to move to the substrate and be quenched before it is trapped, $\mu E \tau_+ > d$, where μ is the hole mobility, E is the average electric field in the film, τ_+ is the trapping time, and d is the film thickness. Using standard relations for mobility and diffusion, $\mu = qD/kT$ and $D = l^2/\tau_+$, where D is the diffusion constant and l is the measured diffusion length, the required electric field is

$$E > \frac{kTd}{ql^2}.$$

In our experiment, $T = 8$ K and $d = 750$ Å, and the value for l is measured in [5] as ~250 Å; this yields $E > 10^3$ V/cm, an order of magnitude larger than the applied electric field. The mechanism for this electric field "amplification" is the removal of electrons, which leaves unbalanced holes in the film. These holes and their image charges in the gold substrate form strong electric fields (an excess hole near the surface of the thin film induces average fields of the order of 10^4 V/cm).

Is the electric field formation a macroscopic or microscopic effect? The hysteresis seen in γ, L, and Y (Fig. 2) depends on beam current and time, suggesting the presence of a macroscopic charging effect. The area of the hysteresis loop decreases with increasing beam current and with slower voltage scan rates. The charge separation, however, occurs primarily per track generated by each incident particle. This conclusion is based on the following observations: (1) there is no transient behavior of the saturation values of γ, L, or Y (on the time scale of ~10 ms) when the beam is removed for as long as 5 s and replaced, indicating that charging is not required for saturation; (2) γ^S/ν, L^S/L^0, and Y^S/Y^0 are independent of beam current over an order of magnitude around the beam currents used for each experiment; and (3) the beam current densities of $\sim 2 \times 10^{12}$ ions/cm^2 s are very low: If we consider the cross-sectional area of an ionization track using the diffusion length of holes (~250 Å [5]), successive arrivals of ions in the same area occur 25 ms apart, and the trapping and recombination times ($\sim 10^{-12}$ s [10]) ensure that the excitations and ionizations created by each incident ion are relaxed long before the next ion arrives. We thus conclude that the primary charge separation and electric field amplification occur on a per track basis, with macroscopic charging accounting for the hysteresis only. The electric field dependence of γ, L, and Y are thus the result of two phenomena acting additively.

In conclusion, we have for the first time separated the contributions of ionization and direct excitation to sputtering and put a lower limit of 45% of total sputtering resulting from ionization events. This separation of contributions to sputtering also confirms that hole trapping must occur for ionizations to begin the electronic relaxation process leading to sputtering and luminescence. The residual sputtering at saturation fields for low S_e incident particles is due primarily to direct excitations to excitonic states augmented by contributions from repulsive ionic states. The observations suggest that electric field amplification inside the Ar film is induced by

removing electrons with a weak externally applied electric field. At low ionization densities this achieves complete charge separation and the corresponding elimination of ionization-initiated luminescence. For high ionization densities, the space charge effect in the track region is too large for the field to overcome, and thus the field has little effect on L or Y. The observations may have implications for radiation damage of other insulators, like biological tissue, in the presence of weak external electric fields.

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