Energy Distribution of Sputtered Metastable Ca Atoms

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The energy distribution of sputtered metastable Ca atoms in the $^3P_2$ sublevel of the lowest-lying triplet state has been measured by Doppler-shift laser-fluorescence spectroscopy. The energy distribution was found to peak at values higher than known for sputtered ground-state atoms. No threshold energy has been found. With increasing oxygen partial pressure the flux of sputtered metastable atoms increased by an order of magnitude; however, the shape of the energy distribution remained unchanged.

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In the last several years a large number of theoretical and experimental attempts have been made to measure and explain the mechanism of inelastic excitations during the sputtering process which leads to the emission of secondary ions and excited particles.[1-8] From experiments studying the light emitted from sputtered excited atoms and molecules it is well known that a fraction of the sputtered particles are ejected in excited states for neutrals as well as for ions. Experimental evidence exists that this fraction can be substantially enhanced by increasing the oxygen coverage on the target.[1,3]

Attempts have been made to determine the energy distribution from the spatial distribution of the emitted light by light-vs-distance (L-D) measurements.[3,4,9] With use of this technique, in many cases extremely high values for the mean velocity of sputtered excited atoms in the range of 100 eV up to 2 keV have been reported.[4,10]

In the last few years the Doppler-shift laser-fluorescence method has been successfully applied to measurements of the energy distributions of sputtered ground-state atoms.[11-16] This technique can be extended to measure the energy distribution of sputtered metastable atoms. The restriction to metastable excited states is due to the fact that all the other excited states will decay before interacting with the laser beam. The first measurements of sputtered metastable particles using this method have been performed on atoms in low-lying metastable fine-structure levels of the ground state of Zr atoms.[17] In this case the energy distributions were found to be identical with those for the ground-state atoms. However, the population of these levels has been found to be higher than expected from a Boltzmann distribution at room temperature. Very recent measurements by Yu, Grischkowski, and Balant[18] on metastable Ba sputtered from BaF_2 and by Schweer and Bay[19] on metastable Fe from metallic Fe are the first direct measurements with Doppler-shift laser-fluorescence spectroscopy (DSLFS) of atoms sputtered in metastable levels with an electronic configuration totally different from that of the ground state.

In this paper we report on energy measurements of metastable Ca atoms sputtered from a Ca metal target. The lowest-lying triplet state of Ca is metastable and 1.9 eV above the singlet ground state. This allows us to detect sputtered metastable atoms in the highest excited state measured by DSLFS so far. Furthermore, the influence of oxygen coverage on the intensity of sputtered metastable atoms and on the shape of their energy distribution will be discussed.

The experimental setup used is outlined in Fig. 1. We used a cw ring dye laser (Coherent 699-21) with a 1-MHz bandwidth to excite the metastable Ca atoms at 616.2 nm. The Ca target has been bombarded with 7-keV Kr^+ ions. The angle of incidence was approximately 45°. With use of diaphragms a sputtered particle beam with a small divergence in the direction normal

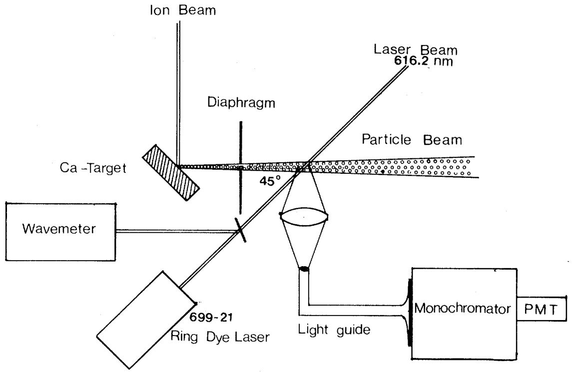

FIG. 1. Experimental setup.

to the ion beam has been obtained. This particle beam was intersected 5 cm in front of the target by the laser beam either at 90° or at 45°. This geometry makes it possible to measure the velocity of the sputtered metastable Ca atoms without taking into account any further geometrical effects when interpreting the spectra. The metastable $^3P_2$ state of Ca (1.89 eV above the ground state) was excited by the laser at 616.2 nm to the $^3S_1$ state. The fluorescence from this state to the $^3P_1$ level separated by 4 nm from the excitation wavelength was registered with a grating monochromator and photon-counting technique. Thus it was possible to work without a lock-in technique. Therefore it was not necessary to chop the ion beam, which turned out to improve the signal stability particulary in the case of higher oxygen partial pressure. This might be attributed to transient effects in the case of chopping.

In recent publications by Wright and co-workers[14,15] questions have been raised concerning the complexity and the difficulties of interpreting DSLFS spectra. In particular, transit-time effects and power broadening were put forward as details which might complicate the interpretation of the spectra quite considerably. In addition, the question as to whether the measured fluorescence signal is proportional to the flux or density of the sputtered particles has been discussed quite extensively. We have used the relations derived by Wright and co-workers with some modifications[20] to calculate the saturation parameter, power broadening, and expected photon yield per atom as a function of its velocity, relevant for the laser system we have used and the atomic constants of the Ca transitions involved in our experiment. A saturation parameter of 15 was obtained indicating that the measurements have been performed in a regime of saturation. These conditions ensure for velocities up to 30 km/sec a constant photon yield per atom independent of the particle velocity. The fluorescence signal therefore is proportional to the particle flux. Power broadening was calculated to be about 40 MHz and can be neglected.

The gas pressure in the chamber was about 5×10^{-10} Torr without ion bombardment. The surface of the Ca target could be monitored by an *in situ* Auger system. The energy spectra of sputtered metastable Ca atoms have been measured in steps from no oxygen partial pressure up to 5×10^{-5} Torr oxygen background pressure. The flux of particles detected in the $^3P_2$ state by DSLFS increased from the oxygen-free case to 1×10^{-5} Torr oxygen partial pressure by approximately one order of magnitude. For further oxygen pressure increase to about 5×10^{-5} Torr the yield remained constant. This is in good accordance with the increase of one order of magnitude that we found by monitoring the light emitted from excited sputtered Ca atoms under 7-keV Kr^+ ion bombardment for the ^1S-^1P resonance transition at 422.6 nm. This shows that metastable excited states with zero electric dipole matrix elements to the ground state and short-lived excited states with a large electric dipole matrix element behave quite similarly. Thus we should expect similar energy distributions. In Fig. 2 we give the velocity spectrum $d\varphi/dv$ for sputtered metastable Ca atoms in the $^3P_2$ state for an oxygen partial pressure of 1×10^{-5} Torr. The velocity distribution peaks at 8 ± 0.1 km/sec (13.4 eV) and the energy spectrum at 6.6 ± 0.2 eV. Sputtered metastable particles with kinetic energies up to 150 eV were measured. The low-energy end of the spectrum does not show an energy threshold within the velocity resolution of our DSLFS spectrometer (less than 500 m/sec), as is usually assumed in the interpretation of L-D measurements.[3,9,10] It is, however, in good accordance with the results obtained for Fe (Ref. 19) and BaF_2 (Ref. 18). The measured velocities in Fig. 2 are considerably higher than for atoms sputtered in the electronic ground state; however, they do not reach the high values proposed earlier for short-lived excited states of Ca.[9] Velocity spectra such as the one shown in Fig. 2 for 1×10^{-5} Torr oxygen partial pressure have been measured for different oxygen coverage. In the range where a sufficiently good signal-to-noise ratio could be achieved

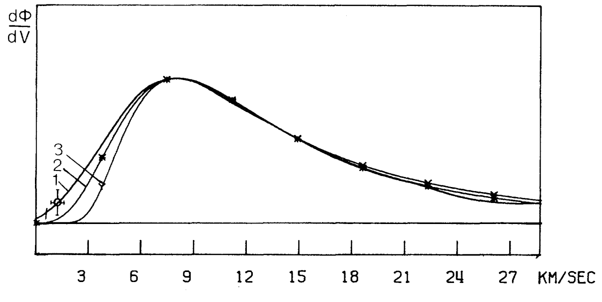

FIG. 2. Velocity spectrum $d\varphi/dv$ of sputtered metastable Ca atoms. Curve 1: measured; curve 2: theoretical $v^3/(v^2+v_b^2)^3$ distribution with $v_b = 8$ km s^{-1}; curve 3: including the survival probability, fitted with $[v^3/(v^2+v_b^2)^3]\exp(-A/av)$ distribution.

(from 5×10^{-7} to 5×10^{-5} Torr) no change in the shape of the velocity distribution was observed even though the yield increased by a factor of 10.

According to linear cascade theory[21] and a planar surface potential barrier the velocity distribution of a sputtered flux of ground-state atoms is of the form $\varphi(v)\,dv \propto v^3/(v^2+v_b^2)^3\,dv$ and peaks at $v=v_b$ or $E=E_b=mv_b^2/2$. E_b the surface binding energy is usually identified with the heat of sublimation.[21] Thus for sputtered ground-state Ca atoms a maximum of the velocity distribution at 1.8 eV or 2.94 km/sec can be assumed. Fitting the much broader velocity distribution of sputtered metastable Ca atoms in Fig. 2 with a $v^3/(v^2+v_b^2)^3$ distribution would yield an E_b of 13.4 eV. However, E_b now can no longer be interpreted as a surface binding energy even though the $v^3/(v^2+v_b^2)^3$ distribution fits the experimental data quite well, with the exception that it gives too low values for low velocities (see Fig. 2).

These results seem to indicate again the large discrepancy between DSLFS and L-D measurements. High threshold energies, as usually assumed, but not directly measurable by the L-D technique, cannot be interpreted in the DSLFS results. L-D measurements can and have been interpreted in terms of an $E/(E+E_b)^3$ distribution,[9] E_b being a fitting parameter indicating the maximum of the energy distribution. An analysis of available L-D results (50 lines for 10 elements) shows a correlation between transition probability γ_i and the derived E_b (or energy threshold) values.[22] E_b varies from above 1000 eV for excited states with a transition probability above 10^8 to values around 10 eV for transition probabilities below 10^7 sec^{-1}. Thus reasonable agreement exists between DSLFS measurements for metastable states ($\gamma_i \lesssim 10^5$ sec^{-1}) and L-D measurements for long-lived excited states ($\gamma_i \lesssim 10^7$ sec^{-1}). It remains open, however, why in L-D measurements for short-lived excited states ($\gamma_i \gtrsim 10^8$ sec^{-1}) such high values for E_b are observed.

Different models have been proposed to explain the sputtering of excited atoms and their dependence on the oxygen partial pressure: (a) Excitations take place inside the bulk and survive further collisions in the collision cascade as has been proposed by Sigmund,[6] or excitations take place only in the last collision. The oxygen dependence of the yield is then explained by blocking of the decay channels by formation of an oxide band gap.[23,24] Thus the survival probability for excited atoms at the surface is proportional to $P_{\text{surv}} \propto \exp(-A/av_\perp)$ (Ref. 7), with $v_\perp$ the normal velocity. We have tried to fit the measured data of sputtered metastable Ca by such a combination of excitation probability in the bulk and deexcitation at the surface, resulting in an even stronger underestimation for low energies than using the pure ground-state distribution (see Fig. 2). (b) In the molecular models[25,26] a different approach is taken. In the case of oxygen adsorbed on the surface, a sputtered surface metal atom and a sputtered adsorbed oxygen atom can form a transient molecule. In general, enough energy is transferred to the molecule to dissociate it leaving the atoms in an ionic or excited state. Such models can account for the increase in sputtered metastable atoms with increasing oxygen partial pressure. Furthermore, the shape of the energy spectrum should be independent of the amount of oxygen coverage as found in our measurements.

In summary, the measurements of sputtered metastable Ca atoms yield an energy distribution with energies considerably higher than for sputtered ground-state atoms. The amount of sputtered metastables is a function of the oxygen coverage of the surface but the form of the energy spectrum is not influenced by oxygen. No energy threshold could be observed. This favors models which do not need deexcitation process at the surface to explain the enhancement with increasing oxygen, but rather models that assume dissociation of sputtered excited molecules.[25,26]

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[1] G. E. Thomas, Surf. Sci. 90, 381 (1979).

[2] P. Williams, Surf. Sci. 90, 588 (1979).

[3] I. S. T. Tsong, in *Proceedings of the Third International Workshop on Inelastic Ion-Surface Collisions, Feldkirchen-Westerham, Federal Republic of Germany, 1980,* edited by E. Taglauer and W. Heiland, Springer Series in Chemical Physics Vol. 17 (Springer, Berlin, 1981), p. 258.

[4] R. J. MacDonald, C. M. Loxton, and P. J. Martin, Ref. 3, p. 224.

[5] R. Kelly, Ref. 3, p. 292.

[6] P. Sigmund, Ref. 3, p. 251.

[7] R. B. Wright and D. M. Gruen, J. Chem. Phys. 72,

147 (1980).

[8] E. Veje, Surf. Sci. 110, 533 (1981).

[9] S. Dzioba and R. Kelly, Surf. Sci. 100, 119 (1980).

[10] S. Dzioba, O. Auciello, and R. Kelly, Radiat. Eff. 45, 235 (1980).

[11] W. Husinsky, R. Bruckmüller, P. Blum, F. Viehböck, D. Hammer, and E. Benes, J. Appl. Phys. 48, 4734 (1977).

[12] W. Husinsky and R. Bruckmüller, Surf. Sci. 80, 637 (1979).

[13] W. Husinsky, R. Bruckmüller, and P. Blum, J. Nucl. Mater. 93&94, 357 (1980).

[14] R. B. Wright, M. J. Pellin, and D. M. Gruen, Surf. Sci. 110, 151 (1981).

[15] R. B. Wright, C. E. Young, M. J. Pellin, and D. M. Gruen, J. Vac. Sci. Technol. 20, 510 (1982).

[16] H. L. Bay, B. Schweer, P. Bogen, and E. Hintz, J. Nucl. Mater. 111&112, 732 (1982).

[17] M. J. Pellin, R. B. Wright, and D. M. Gruen, J. Chem. Phys. 74, 6448 (1981).

[18] M. L. Yu, D. Grischkowski, and A. C. Balant, Phys. Rev. Lett. 48, 427 (1982).

[19] B. Schweer and H. L. Bay, Appl. Phys. A 29, 53 (1982).

[20] For the calculation of the saturation parameter S the formulas (7), (10), and (16) from Ref. 14 were used; however, in formula (10) Δr_s was substituted by Δr from Eq. (13). The power- and transit-time-broadened Δr_s was obtained by $\Delta r_s = \Delta r(1+S)^{1/2}$ instead of Eq. (12) in Ref. 14.

[21] P. Sigmund, Phys. Rev. 184, 383 (1969).

[22] G. Betz and W. Husinsky, to be published.

[23] W. F. Van der Weg and P. K. Rol, Nucl. Instrum. Methods 38, 274 (1965).

[24] C. B. Kerkdijk and R. Kelly, Surf. Sci. 47, 294 (1975).

[25] G. E. Thomas, Radiat. Eff. 31, 185 (1977).

[26] G. Blaise, Surf. Sci. 60, 65 (1976).