Rotational and vibrational excitation of sputtered silver dimers

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Abstract. The internal excitation of silver dimers sputtered from a polycrystalline silver surface by \( \text{Ar}^+ \) ions of 5 keV was investigated by one color resonant two photon ionization spectroscopy and time-of-flight mass spectrometry. From the resulting spectra, vibrational and rotational population temperatures around 3000 K and 7000 K are determined which agree well with corresponding predictions obtained from molecular dynamics simulations of the molecule sputtering process.

Introduction

It is well known that the flux of particles sputtered from a solid metal surface by energetic ions contains atoms as well as molecules. The fundamental processes leading to the formation of sputtered molecules and clusters are still not completely understood. In the so-called linear cascade regime of the sputtering process, the atomic ejection following a primary ion impact event is caused by elastic collisions between the atoms in a subsurface region of the bombarded solid, and hence the molecule formation will also be collision-dominated. Various theoretical model descriptions of cluster sputtering have appeared in the literature ranging from conceptually simple statistical considerations to fairly sophisticated molecular dynamics computer simulations (1). Some of these models allow predictions of the internal energy distribution of sputtered clusters, and it has even been suggested that this distribution may serve to distinguish between the different molecule formation mechanisms.

Bombardment of metallic samples with rare gas ions of energies in the keV range is often regarded as a model case of collisional sputtering (2). As a consequence, the internal energy stored in a sputtered metal dimer and its distribution among the various rotational and vibrational states may put an interesting test to the above-mentioned models. Corresponding experimental data, on the other hand, exist only for a few alkali dimers (3) (Na\(_2\), K\(_2\) and Cs\(_2\)), where thermal distributions with internal population temperatures of around 1000 K were found. Due to the very low melting temperature of the respective metals, however, it is not clear in how
far thermal effects contribute to the sputtered flux in these cases. In the present paper, we therefore investigate the internal excitation of sputtered silver dimers, since, due to its high melting point, the sputtering of silver represents an almost ideal example of collisional sputtering.

Experimental

The experiments were performed using a reflectron time-of-flight mass spectrometer described in great detail elsewhere (4). A MARZ grade polycrystalline silver sample was bombarded under 45° with a pulsed 5 keV Ar⁺ ion beam of 5 μA. After the end of the primary pulse, a pulsed laser was fired, whose beam of approximately 1 mm diameter was directed parallel to the sample surface at a distance of approximately 1 mm, and sputtered neutral silver dimers generated during the primary ion pulse were ionized by a resonant two photon ionization (R2PI) scheme described below. The photo-ionized molecules were extracted towards the mass spectrometer which allowed the isotope-selective detection of Ag₂⁺ ions.

Details of the spectroscopic setup are given elsewhere (5). Briefly, a one-color two photon ionization process was used involving a resonant transition from the Ag₂ X'Σ₉⁺ ground state to the Ag₂ C σΠ₉ state and a non-resonant transition from this state to the Ag₂⁺ ionization continuum. The frequency doubled photon beam generated by an excimer pumped dye laser (Lambda Physik LPD 3002) was shaped such that its spatial FWHM matched the sensitive volume of the mass spectrometer (approximately 1 mm in diameter). The laser pulse energy was monitored by a fast photodiode and kept constant during a wavelength scan by a variable dielectric attenuator located in the pump beam path.

The ion signals were detected by a boxcar integrator, whose gate delay was set to the appropriate flight time of the heteronuclear ⁴₁⁰⁶Ag₂ isotopeomer. The gate width (50 ns) was chosen to ensure integration over the corresponding flight time (or mass) peak.

Results and discussion

Fig. 1a shows a typical R2PI spectrum of the silver dimer signal. The laser wavelength was scanned in steps of 5 pm and the signal of the ⁴₁⁰⁶Ag₂⁺ photoions, averaged over 1000 laser shots, was detected for a laser pulse energy of 1.5 μJ (corresponding to a peak power density of approximately 10⁴ W/cm²). The laser intensity was kept constant within ±15 % rms throughout the whole scan. In addition, the data were normalized to the laser power density measured at each wavelength in order to reduce the statistical noise. The broad feature centered around λ = 266 nm observed in the spectrum is due to the X-C transition of the
A\textsubscript{g}_{2} molecule. The apparent lack of well resolved vibrational bands already indicates a high degree of internal excitation of the sputtered silver dimers. The interpretation of the measured spectra in terms of vibrational and rotational excitation of the sputtered neutral dimers was done as follows. First, Boltzmann distributions were assumed for the population of internal states with independent vibrational and rotational temperatures \( T_{\text{vis}} \) and \( T_{\text{rot}} \), respectively. Then, measured spectra were simulated by calculating term values and two-photon ionization probabilities for all possible ro-vibrational transitions between the ground state and the intermediate state, convoluting the resulting lines with a Gaussian of fixed width corresponding to the laser linewidth (5 pm) and sorting the resulting spectrum into wavelength slots of 5 pm width. The term values of allowed ro-vibrational transitions between the \( X \) and the \( C \) state were calculated by a standard Dunham expansion using spectroscopic values of \( \omega_x, \omega_{\text{et}}, B_x, \alpha_x, \) and \( D_x \) taken from the literature (6). In order to obtain reasonable agreement with measured spectra, it was found necessary to include the effect of saturation into the simulation. Hence, absolute values of the transition rate

\[
R_{\text{exc}} = B_{X\text{C}} \rho_{\text{exc}} \cdot FCF(\nu'', \nu') \cdot HLF(J'', J')
\]

between ro-vibrational levels \( \nu'', J'' \) and \( \nu', J' \) of the \( X \) and \( C \) state are needed. In eq. 1, \( B_{X\text{C}} \) denotes the Einstein coefficient which may be parametrized by the total oscillator strength \( f_{X\text{C}} \) of the \( X-C \) transition, \( \rho_{\text{exc}} \) is the spectral energy density of
the excitation laser and $FCF$ and $HLF$ are the Franck-Condon and HönL-London factors of the vibrational and rotational transitions, respectively. While the $HLF$ values were taken from the literature (7), the Franck-Condon factors were calculated from Morse potential fits to the spectroscopic constants (5). Since no literature data are available for the second rotational constant $D'_r$ of the C state, we used the Kratzer relation to obtain the respective value. The ionization probability $P_i$ of a ground state molecule with the excitation/ionization laser tuned to a resonant $X$-$C$ transition was calculated from standard rate theory of two photon ionization (5,8). A series of simulated spectra were calculated using $T_{vib}$, $T_{rot}$ and $f_{XC}$ as parameters. The values of $T_{vib}$ and $T_{rot}$ were varied independently from each other between 1000 K and 9000 K in steps of 1000 K, while the values of $f_{XC}$ were changed between 1 % and 10 % in steps of 2.5 %. The resulting set of simulated spectra was then compared to the experimental data by evaluating the sum of the squared deviations between simulated and experimental spectra. Fig. 1b shows the optimal spectrum fitted to the data displayed in fig. 1a, which was obtained using $T_{vib} = 3000$ K, $T_{rot} = 7000$ K and $f_{XC} = 7.5$ %. Hence, the experimental data clearly reveal that the sputtered silver dimers are hot, i.e. are formed with internal temperatures of several thousand Kelvin. This finding as well as the absolute temperature values are in very good agreement with recent theoretical molecular dynamics simulations (9) of silver dimer sputtering, which predict values of $T_{vib} = 3500$ K and $T_{rot} = 6800$ K. The apparent difference between the vibrational and rotational population temperatures of the sputtered dimers emphasizes the non-equilibrium character of the sputtering process which is due to the fast time scale ($\sim 10^{-13}$ s) on which atomic collisions leading to the sputter ejection of particles occur.

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References