Anomalous Sputtering Behavior Observed by Quantitative Measurements of the Population Partition of Metastable Ni Atoms

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The population partition of metastable atoms after ion beam sputtering of polycrystalline Ni was studied. Resonant multiphoton ionization using double resonant two-color two-step photoionization was used. This allows the quantitative measurement of the relative population of all metastable states. The high lying metastable states with excitation energies around 2 eV show populations of the order of 10% of the ground state population which is several orders of magnitude higher than expected. The anomalous population partition is interpreted in the resonant electron tunneling model. [S0031-9007(96)02032-7]

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The fundamental physical processes governing ion beam sputtering can be studied experimentally by examining the ejected particles. The inelastic collisions of energetic ions with solid surfaces result in the ejection of atoms or clusters in different charge states and in different states of electronic excitation. Both the experimental and theoretical situations have been reviewed by Yu [1]. It is generally assumed that the fraction of sputtered atoms on highly excited *metastable* states is very low [2–4]. This assumption is based on quasithermal excitation and nonradiative deexcitation which depend strongly on the excitation energy.

However, theoretical models and, albeit scarce, experimental evidence for a substantial population of such states are available. Indeed, the electron transfer model of Veje [5] predicts strong population of all states within an atomic excitation energy window corresponding to the valence band of the solid under study. Experimentally, in a study of Fe atom sputtering using laser induced fluorescence, a considerable population of metastable states at about 1 eV excitation energy was observed [6,7]. Measurements based on fluorescent photon detection, however, suffer from limited sensitivity and can therefore not be generally applied.

Recently, studies of population and kinetic energy distributions of sputtered metastable Ni atoms, using resonant ionization spectroscopy (RIS) [8], were reported [3,4]. However, the experimental procedure used in these investigations limited the study of metastable states to excitation energies below 0.5 eV. Also recently, RIS was applied to probe the population of one high lying metastable state of sputtered Ag atoms; a population of about 6% of the ground-state population was deduced from the data [9,10]. The observations on sputtered Ni and Ag were interpreted as evidence for the fact that the sputter yield of metastable atoms depends on the electronic structure of both the solid and the sputtered atom.

In this Letter we report on the development and application of a very sensitive experimental procedure for the quantitative measurement of relative populations of *all* metastable states. The method is based on resonant multiphoton ionization spectroscopy using two-color two-step ionization schemes in combination with time-of-flight mass spectrometry. Application of this technique to the study of metastable Ni atoms produced by Ar^+ sputtering of a polycrystalline foil is reported. The measurements revealed that the population of metastable states with excitation energies above 1.5 eV is anomalously high. Such populations can be interpreted within a resonant electron tunneling approach [5].

The experimental procedure and setup will be presented in detail elsewhere [11]. Here we give a brief description of the apparatus and the most important aspects of the experimental procedure for measuring population distributions. The setup is constructed around a UHV chamber (base pressure about 6×10^{-10} hPa). The plasma ion source produces Ar ions that can be electrostatically accelerated onto a target foil with energies ranging from 3 to 15 keV. Both pulsed and continuous operation of the ion gun are possible. The sputtered neutral atoms are resonantly laser ionized and accelerated into a reflection type time-of-flight mass spectrometer and subsequently counted by a dual microchannel plate detector. The present experiments are carried out with a continuously impinging ion beam. With the use of relatively large laser beam diameters (typically 1 mm) and short laser pulses (6 ns), the measured populations correspond to the number density within the ionization volume. This means that our measurements do not directly reflect the relative sputtering yields if atoms ejected in different states have different kinetic energy distributions.

Before each measurement, the ion beam is continuously rastered across the Ni foil, assuring the sputtering spot to be clean. The purity of the foil was verified by secondary ion mass spectrometry (SIMS). Within the sensitivity of the method no contaminants could be detected after the rastering procedure. Furthermore, the SIMS Ni^+ yield decreased drastically as expected for removal of an oxidized layer [12].

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Our *new experimental procedure* is based on two-color two-step resonance ionization with a first step resonantly exciting the metastable atoms to an intermediate state and an independent second ionization step. The *same intermediate state* is used for photoionization sequences starting from a subset of metastable states. This implies that the measured relative photoion intensity will be directly proportional to the initial relative population of the states if the different excitation steps are saturated, which can easily be obtained with moderate laser pulse energies in most cases. In order to optimize the ionization efficiency, a resonant transition to an autoionizing state is used as an ionization step. To address all metastable states, several intermediate states with different angular momenta have to be employed for most elements [8].

The procedure is exemplified in Fig. 1 where a partial level scheme of Ni I is presented, showing all metastable states and the chosen triplet of intermediate states ($^3F^0_{2,3,4}$), together with the excitation steps [13]. A wide spectral range is needed for the different two-color two-step excitations. We are using an optical parametric oscillator [Spectra-Physics (SP) MOPO 730] pumped by a Nd:YAG laser (SP GCR 230-10) and equipped with a frequency doubling option (SP FDO) delivering continuously tunable laser light from 225 nm up to 1600 nm. For the ionization step a tunable dye laser (SP PDL-3) with wavelength extender (SP WEX) and also pumped by a Nd:YAG laser (SP GCR-12) is used. Both systems provide pulsed laser light (about 6 ns, 10 Hz) with a near-Gaussian beam profile and with bandwidths ranging from 6 to 15 GHz and pulse energies ranging from 4 to 50 mJ per pulse.

Several series of experiments were performed in order to determine the saturation behavior of both the excitation and ionization steps [11]. Saturation of the excitation steps could be obtained for all transitions shown in Fig. 1 with the laser focused to a cross section of typically 3 mm^2 and with pulse energies of about 1 mJ per pulse. This is illustrated in Fig. 2 where the typical saturation behavior of two transitions is exemplified. Only well saturated transitions were used for the extraction of relative population values. The ionization steps were saturated by tuning the ionizing laser to resonant transitions into autoionizing states situated just above the ionization limit [14]. This strongly enhances the sensitivity of our method and not only enables us to study states with low population, but also allows us to measure kinetic energy distributions of these states [11].

In order to check both the validity and the accuracy of the experimental procedure, a population distribution measurement was performed for thermally produced Ni atoms. Therefore a Ni filament was introduced into the UHV chamber and electrically heated to 1470 ($\pm$100) K. The filament temperature was measured with a pyrometer. Populations of the low lying states relative to the ground-state population were obtained and are presented in a semilogarithmic plot in the lower part of Fig. 3. These data were fitted with the Maxwell-Boltzmann distribution, yielding a temperature of 1550 ($\pm$100) K, in excellent agreement with the pyrometric measurement.

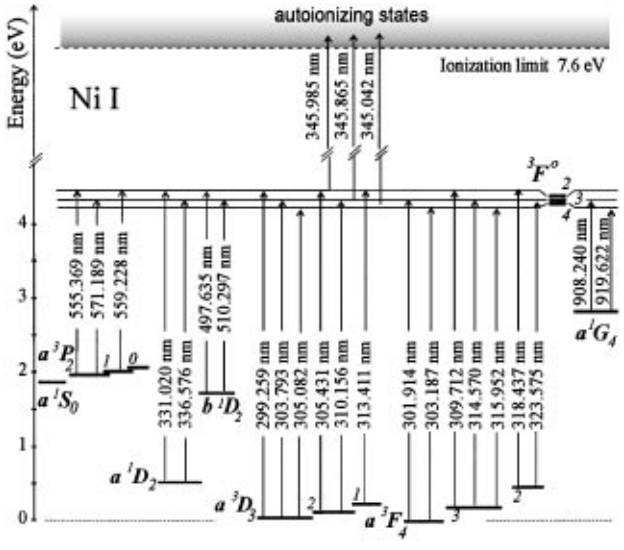

FIG. 1. Partial level scheme of Ni I. All metastable states and the employed intermediate multiplet are shown. The excitation and ionization steps that are used for the population partition measurements and their wavelengths are indicated.

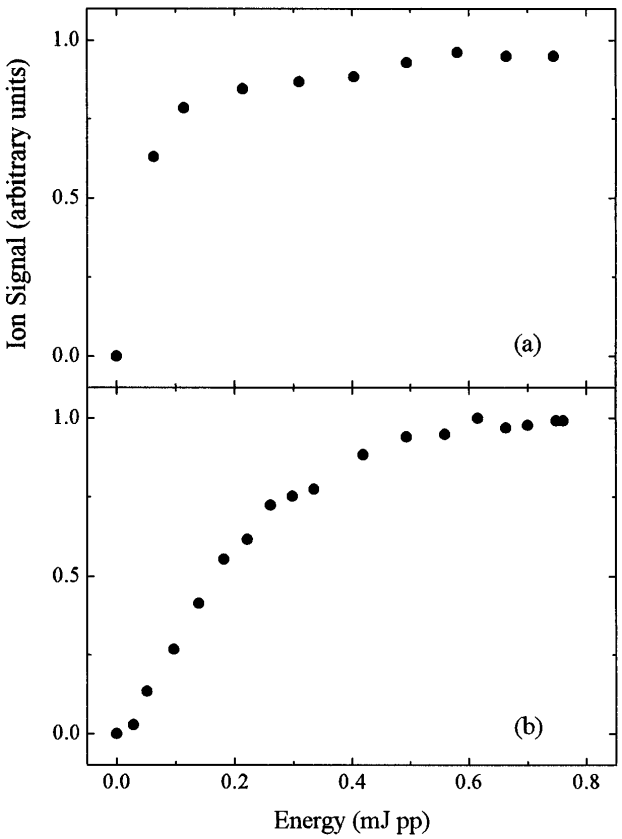

FIG. 2. Saturation behavior of the excitation transitions $a^3D_3 \rightarrow {}^3F^0_3$ (a) and $a^3P_2 \rightarrow {}^3F^0_3$ (b) as a function of excitation laser energy with fixed ionization laser energy.

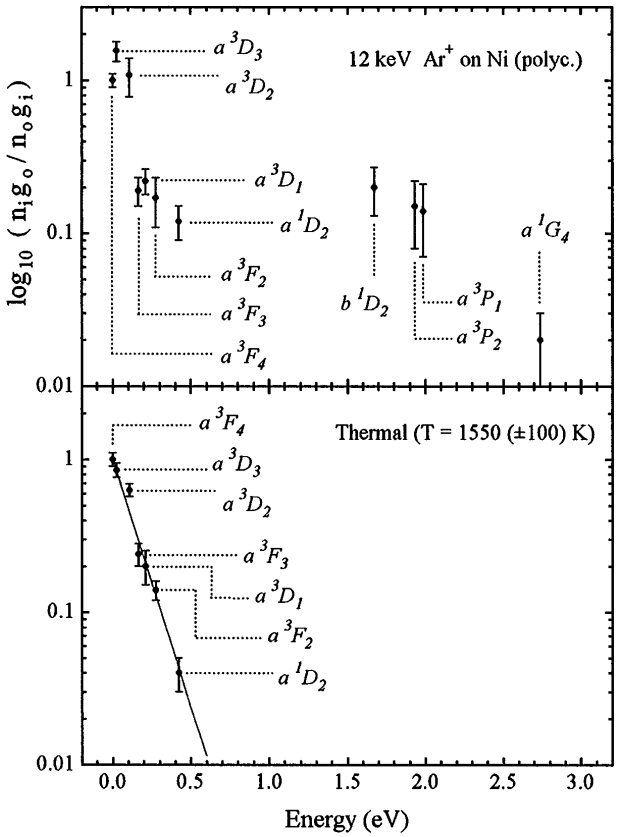

FIG. 3. Population distribution of Ni metastable states for atoms produced by thermal sublimation of a wire (lower part) and by 12 keV Ar^+ sputtering of a polycrystalline foil (upper part). The populations (n_i) are given relative to the ground state and corrected for statistical weight (g_i).

In the figure averages from four independent measurements, each involving one to three intermediate states, are given. To determine the errors not only the standard deviation on this mean value has to be considered. For some ionization schemes, a background due to one-color two-step ionization has to be subtracted. Because of the slightly different ionization volume for this process, a state dependent additional error of about 10% has to be added. The thermal data can be used to quantify systematic errors due to possible incomplete saturation behavior of certain excitations. The good agreement of the data with the fitted Maxwell-Boltzmann distribution shows that no such deviations are present within the estimated uncertainties.

At this point a comparison with the earlier multiphoton ionization studies on sputtered Ni [3,4] and Ag [9,10] should be made. In the former experiments, only the first excitation step of the laser ionization process could be tuned to a resonant transition, while the second ionization step is made by a photon of the same laser pulse. Because of the presence of a complex structure of autoionizing states, the ionization cross sections are strongly wavelength dependent, which results in a scattering of ionized particle intensity of typically 1 order of magnitude if different excitation transitions starting from the same state are used. In one experiment by He *et al.* [4] this was partially circumvented by calibrating the different ionization cross sections using the data of a separate reference measurement on a thermally distributed ensemble; this procedure, however, fails for highly excited states as the thermal populations of these states are far below the RIS detection limit. In the Ag experiment, ionization schemes with strongly different saturation behavior were used for the ground state and the metastable state, which makes the derived relative population dependent on theoretical assumptions about these saturation behaviors. None of these drawbacks are present in our approach, where the relative populations follow directly from the measured photoion intensities.

The experimental procedure was applied for measuring the population distribution of Ni atoms produced after Ar ion beam sputtering of a polycrystalline foil. As sputtering energies both 3 and 12 keV were used. The data for 12 keV are shown in the upper part of Fig. 3. Within the experimental error no difference in the population of the 3 keV data could be noticed. Two remarkable and distinct features show up. (i) A population of the order of 10% for high lying states with excitation energies from 1.6 to 2.7 eV is apparent. (ii) For the low lying states a population inversion favors the states with electron configuration $3d^9 4s^1$ with respect to the ground-state configuration $3d^8 4s^2$. Indeed the excited states a^3D_3 and a^3D_2 are populated about 60% more than the ground state a^3F_4.

The population of the states b^1D_2, a^3P_2, and a^3P_1 is as high as the population of the low lying states a^3F_3, a^3F_2, a^3D_1, and a^1D_2, which is several orders of magnitude higher than commonly expected. A model for the sputtering of atoms into highly excited states was proposed by Veje [5]. Taking into consideration the transition from electron valence band states into final atomic states, it is assumed that both the orbital energy and shape are preferentially preserved when an electron is captured by an ionic core while escaping from the surface. In this case one expects favored population of atomic states with a binding energy close to the binding energy of the valence electrons in the solid. Also the states with wave functions having good geometric overlap with the surface electron states will be preferentially excited. In the case of Ni with a work function of 5.2 eV, energy matching is fulfilled for excitation energies lower than 2.5 eV. This means that there is a very good overlap for the states b^1D_2, $a^3P_{1,2}$ while the state a^1G_4, which is much less populated, falls just outside. Although our results can be interpreted as supporting evidence for this model, more experiments on different systems will be needed to verify the general applicability of this model.

It has also been argued that excited states might be populated by photodissociation of Ni dimers and subsequent ionization by the same laser pulses [3,15]. However, this is in variance with time-of-flight measurements yielding significantly different distributions for Ni dimers and the highly excited states [11].

The observed population inversion of the low lying states is similar to, but less pronounced than, the recently reported measurements of He *et al.* [4], who examined the sputtering of single crystalline Ni and observed a population inversion of about 500%. The preferential population of the a^3D_J multiplet was attributed to the close correspondence of its $3d^9 4s^1$ electron configuration with the Ni band structure. Although the experimental procedures of both experiments are quite different, the only physical difference in the two collision studies is the crystal structure of the metallic Ni target. Should this be the reason for the very different behavior of the population distributions, then the influence of the crystal orientation and the differences in electronic band structure along various crystal orientations may play a major role, and even more pronounced effects should be expected for atoms emitted from single crystals along distinct crystal axes.

In conclusion, we reported the first application of an experimental procedure based on resonant multiphoton ionization which allows the quantitative measurement of population distributions of sputtered neutral atoms over all metastable states. For 12 keV Ar^+ sputtering of polycrystalline Ni, high populations of the order of 10% of states with excitation energies around 2 eV were measured. Our results clearly demonstrate that nonthermal effects dominate the atomization by ion-beam sputtering. The electronic configuration continues to play a decisive role in metastable state population for high excitation energies. The high sensitivity and the general applicability inherent to resonance ionization will enable us to study different elements both in pure form and as impurities in different matrices. This will allow us to deconvolute the influence of the bulk electronic structure from statistical collisional and excitation-deexcitation processes in the metastable state population and to further examine the possible descriptions for excitation during sputtering, such as valence electron transfer models.

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