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Influence of the atomic structure on the quantum state of sputtered Ir atoms

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The probability of the ejection of a neutral atom in a specific quantum state after keV-ion beam sputtering is often interpreted in terms of the interaction between the atomic states of the escaping atom and the electronic states of the solid. In this work, we examined this interplay in the sputtering of iridium as this element has—unlike the elements employed in previous investigations—a complex atomic structure due to strong configuration interactions. Double-resonant two-photon laser ionization is used to probe the sputtered Ir atoms yielding information about the probability for an ejected atom to populate a specific atomic state and its escape velocity. The qualitative features of the corresponding population partition and state-selective velocity distributions show the influence of the excitation energy and the electronic structure of the different atomic states. A comparison is made between the experimental data and predictions from the resonant electron transfer description.

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I. INTRODUCTION

The collision of a swift atomic particle with a metallic surface leads to the ejection of surface atoms, the so-called sputtering process. For already several decades, the electronic processes during sputtering, which cause a distribution of the sputtered atoms over different quantum states, form the intriguing subject of many experimental and theoretical investigations of which an overview can be found in Ref. [1]. Key information about the electronic processes during sputtering can be found in the probability for a sputtered neutral atom to populate a specific quantum state and the velocity dependence of this population probability. Therefore the population partitions and state-selective velocity distributions of sputtered atoms in different states already have been reported for quite a number of transition metals [1].

First investigations showed that the population of a specific atomic state after sputtering is determined by the excitation energy [2]. Later, it was recognized that also the electron configuration of the quantum state influences to a large extent the velocity-dependent population of the different atomic states [3,4]. Recent investigations on the sputtering of atoms in metastable states from several pure transition metals showed that it in fact is the interplay between the atomic electron configuration and the bulk electron configuration of the bombarded solid that determines the final state of the ejected particles [5–7]. These latter investigations had in common that the ground and metastable states of the employed transition metals (Co, Ni, and Cu) have a rather simple electronic structure, i.e., the configuration interaction between atomic states is weak and the degree of level mixing is not significant. A single electron configuration could be assigned to all probed atomic states.

We investigated whether the interpretation based on the coupling between atomic and metallic levels can also be applied to sputtering of elements of which the atomic states have a more complex nature, i.e., elements that experience a strong configuration interaction. An example of such an element is iridium. Ir experiences strong spin-orbit interactions, which implies strong configuration interactions: Pure *Russel-Saunders* coupling no longer holds, the total orbital angular momentum L and the total spin S no longer are good quantum numbers, and the atomic levels are configuration mixed [8]. We present experimental data on the relative population and state-selective velocity distributions of Ir atoms sputtered in the ground state or in one of the six lowest-lying metastable states. These data are obtained by state-selective probing of the sputtered Ir atoms with double-resonant laser ionization mass spectrometry. A thorough analysis of these experimental results will clarify whether the sputtering of atoms that experience strong level mixing also can be interpreted by the interplay between the electronic structures of the atom and the metal.

II. EXPERIMENTAL PROCEDURE

The experimental apparatus is described in detail elsewhere [6]. An ion gun directs 13-keV Ar^{+} ions at 45° incidence onto an polycrystalline Ir foil (Goodfellow, purity 99%) located centrally in an UHV vessel with a base pressure below 3×10^{-10} mbar. The ion beam irradiates the target either continuously or in pulses with a pulse duration down to 100 ns. The plume of sputtered particles is intersected 4 mm in front of the target foil by two overlapping laser beams, slightly defocused to a diameter of about 1 mm. The two tunable laser systems, an optical parametric oscillator and a dye laser, both pumped by independent Nd:YAG lasers, generate linearly polarized pulsed laser light with a pulse length of 6 ns covering the wavelength range from 225 to 1600 nm and with pulse energies of about 5 mJ in the UV region and a linewidth of approximately 15 GHz. The atoms sputtered in a polar angle interval of 7° around the surface normal can be photoionized and subsequently accelerated into a reflectron time-of-flight mass spectrometer for

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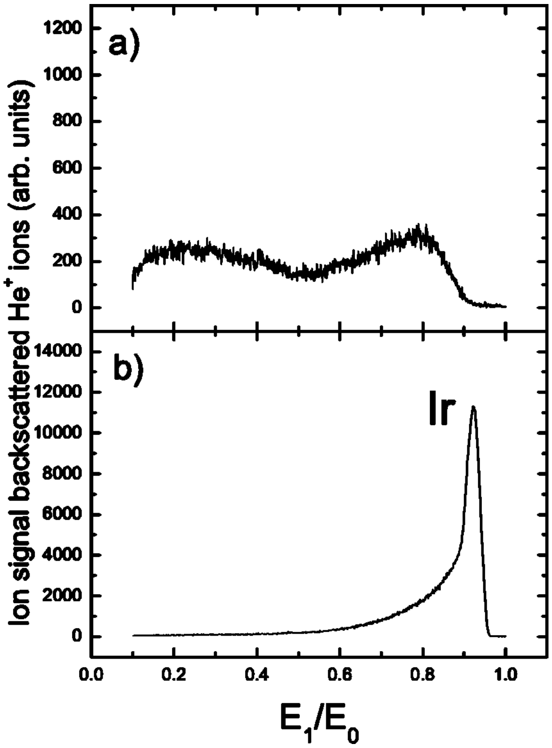

FIG. 1. LEIS spectra obtained after scattering of 2-keV He$^+$ ions from the Ir sample before (a) and after (b) sputter cleaning of the sample.

mass-selective detection. Prior to each experiment, the target foil was subjected to prolonged sputter cleaning to remove any surface contaminants. This cleaning procedure was evaluated by *low-energy ion scattering* (LEIS) experiments. This technique allows us to determine the surface composition of the Ir sample by measuring the scattering of He$^+$ ions as a function of the ratio of the kinetic energy of the He$^+$ ion after (E_1) and before ($E_0 = 2$ keV) scattering. The LEIS spectrum before sputter cleaning [see Fig. 1(a)] shows broad and vague features that are typical for oxidized metal surfaces contaminated with Na, K, and hydrocarbons. Figure 1(b) shows the LEIS spectrum after a prolonged ion bombardment to sputter clean the target. An intense peak characteristic for He$^+$ ions scattered of Ir atoms is observed, representing a pure, uncontaminated surface. To probe the Ir atoms sputtered in the ground state and the lowest-lying metastable states, an experimental procedure based on two-color two-step resonance laser ionization was used. Details of this experimental procedure can be found elsewhere [6]. Here, we only sketch the main aspects of the ionization procedure. In the first step, atoms in one of the envisaged states are excited into an intermediate state by photon absorption. In the second step, the absorption of a second, independent photon ionizes an atom in the intermediate state. To increase the efficiency of this state-selective photoionization procedure, the second step can be tuned to reach an autoionizing state, which is a bound state above the ionization potential mostly stemming from inner-shell excitations or multiple-electron excitations. As such, also the second step becomes a bound-bound transition and the overall ionization probability can be enhanced by several orders of magnitude [9,10]. For this purpose, an exploration of the ionization continuum of Ir was performed to search for suitable autoionizing states to employ in the ionization procedure of sputtered Ir atoms [11].

To measure the population partition of sputtered Ir atoms, the ion beam is operated in the long pulse mode (13 μs), which ensures that atoms with all velocities are present in the ionization volume defined by the two overlapping laser beams. When possible, the same intermediate state was used to directly deduce the relative population from the relative photoion signals, regardless of the ionization efficiency. Only saturation of the excitation transition is needed, which already is obtained at a moderate laser fluence of the order of 5×10^{15} photons/cm^2 [11]. Due to the extended range of values for the total angular momentum J in Ir, selection rules governing optical transitions prohibit that the populations in all metastable states are probed via a single intermediate state. The overall population partition is then obtained by combining the partial partitions of overlapping subsets of metastable states. By tuning the ionization procedure into an autoionizing state, also the ionization transition can reach saturation. This reduces the uncertainty on the photoion signal substantially as fluctuations in laser fluence now only induce small variations in the measured photoion signal [11].

To measure the velocity distributions of atoms sputtered in a specific atomic state, short ion pulses of 300 ns are applied to the target. The delay time between the ion pulse and the ionizing laser pulses corresponds with the flight time that the sputtered particles need to travel the fixed distance between the sample surface and the ionization volume. Therefore the delay time is determining the velocity of the atoms present in the ionization volume and as such, the ionization procedure becomes velocity selective.

III. EXPERIMENTAL RESULTS

We probed Ir atoms sputtered in the ground state and the six lowest-lying metastable states of which the relevant properties are listed in Table I. The partial energy-level diagram of neutral Ir including the transitions employed to ionize the atoms sputtered in these atomic states is presented in Fig. 2. The population partition of Ir atoms sputtered in the ground state and the lowest-lying metastable states is shown in Fig. 3. The data are corrected for the degeneracies of the atomic states and normalized to the population of the ground state. All six metastable states show a substantial relative population between 3% and 12%. Overall, one can state that the relative population on the states decreases with increasing excitation energy. The relatively high population on the excited states (with excitation energies up to 1.22 eV) is another manifestation of the well-known fact [1] that nonthermal effects dominate the sputtering of particles in different atomic states. Examples of the velocity distributions of Ir atoms sputtered in the ground state $|9/2\rangle$ and in some of the metastable states ($|9/2\rangle'$ and $|7/2\rangle'$) are presented in Fig. 4(a). The velocity distribution of atoms sputtered in the first excited state $|9/2\rangle'$ peaks at a higher velocity and is broader than the velocity distribution of the atoms sputtered in the ground state $|9/2\rangle$. The velocity distributions of atoms in the

TABLE I. Lowest-lying atomic states of Ir employed in this investigation. Due to configuration interaction, only the *J* value is a good quantum number and is therefore chosen to represent the atomic states. The tabulated designation is used throughout the text to identify the different atomic states. The composition of the different atomic states is according to Ref. [8]. Only the most dominant contributions are given.

Excitation energy (eV)	J	Designation	LS state	Contribution
0.00	9/2	$\lvert 9/2\rangle$	$5d^7\,6s^2\,{}^4F$	0.84
			$5d^7\,6s^2\,{}^2G$	0.14
0.35	9/2	$\lvert 9/2\rangle'$	$5d^8\,6s^1\,{}^4F$	0.96
0.51	3/2	$\lvert 3/2\rangle$	$5d^7\,6s^2\,{}^2P$	0.36
			$5d^8\,6s^1\,{}^2P$	0.18
			$5d^8\,6s^1\,{}^2D$	0.15
0.72	5/2	$\lvert 5/2\rangle$	$5d^8\,6s^1\,{}^2F$	0.27
			$5d^7\,6s^2\,{}^4F$	0.20
			$5d^7\,6s^2\,{}^2D(2)$	0.12
0.78	7/2	$\lvert 7/2\rangle$	$5d^8\,6s^1\,{}^4F$	0.53
			$5d^8\,6s^1\,{}^2F$	0.27
			$5d^7\,6s^2\,{}^4F$	0.15
0.88	7/2	$\lvert 7/2\rangle'$	$5d^7\,6s^2\,{}^4F$	0.81
			$5d^8\,6s^1\,{}^4F$	0.13
1.22	5/2	$\lvert 5/2\rangle'$	$5d^7\,6s^2\,{}^4F$	0.40
			$5d^8\,6s^1\,{}^4F$	0.19
			$5d^8\,6s^1\,{}^4P$	0.18

other probed atomic states are identical within the experimental uncertainty and are exemplified in Fig. 4(a) by the velocity distribution of the metastable state $\lvert 7/2\rangle'$. The latter distributions are shifted to lower velocities compared with the velocity distributions of atoms in the ground state and the first excited state. The velocity distribution of the whole ensemble of detected neutral sputtered particles, obtained by summing all the velocity distributions weighted by their relative population, is shown in Fig. 4(b). According to linear collision cascade theory and with the reasonable assumption that the fraction of atoms sputtered in ionic states or other excited neutral states is negligible, the experimentally determined velocity distribution can be approximated by the Thompson distribution $f(v)$:

$$f(v) \propto \frac{v^3}{\left(\dfrac{mv^2}{2} + U_0\right)^3} \tag{1}$$

in which U_0 represents the surface binding energy [12]. Empirically, it was observed that the surface binding energy is of the order of the sublimation energy. Figure 4(b) indeed shows a good agreement between the experimental distribution and the fitted Thompson distribution with a surface binding energy U_0 of 7.0(5) eV, close to the sublimation energy of Ir (6.9 eV).

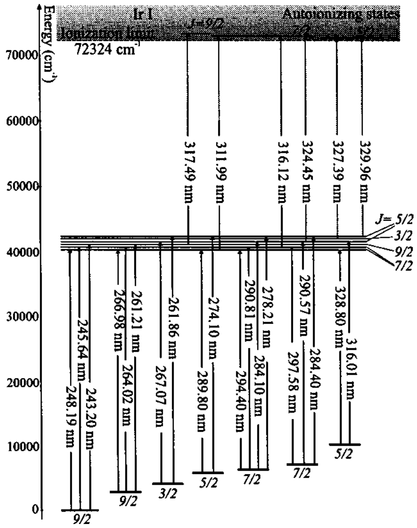

FIG. 2. Partial energy-level scheme of neutral Ir. Indicated are the transitions used to probe the atoms sputtered in the lowest-lying states.

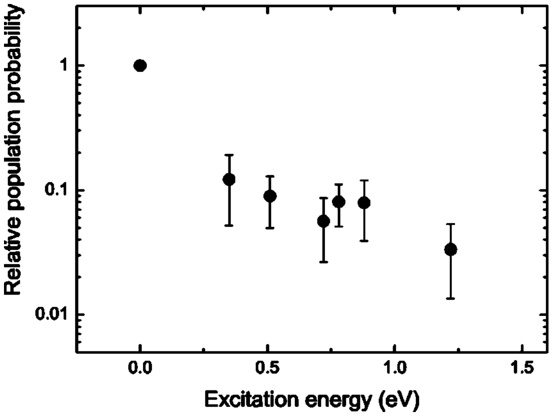

FIG. 3. The relative population on the different atomic states of Ir after ion-beam sputtering, corrected for the statistical degeneracy of the states.

IV. DISCUSSION

To interpret the various observations about sputtering in different atomic states, different electronic processes such as dimer dissociation, collisional excitation at or above the surface, and nonradiative deexcitation have been invoked. In recent reports, we presented the population partitions and state-selective velocity distributions of Co, Ni, and Cu atoms sputtered from the corresponding pure metal in the ground state and in all metastable states [6,7]. A first general observation was that atomic states with a $3d^x\,4s^1$ electron configuration ($x=8,9,10$ for, respectively, Co, Ni, and Cu) had a relatively higher probability to become populated during sputtering compared to the atomic states with a $3d^{x-1}\,4s^2$ electron configuration. A second observation was that the velocity distributions of atoms in atomic states with a $3d^x\,4s^1$ electron configuration were systematically shifted to higher velocities compared to the velocity distributions of atoms in atomic states with a $3d^{x-1}\,4s^2$ electron configuration. Analog independent investigations on the sputtering of

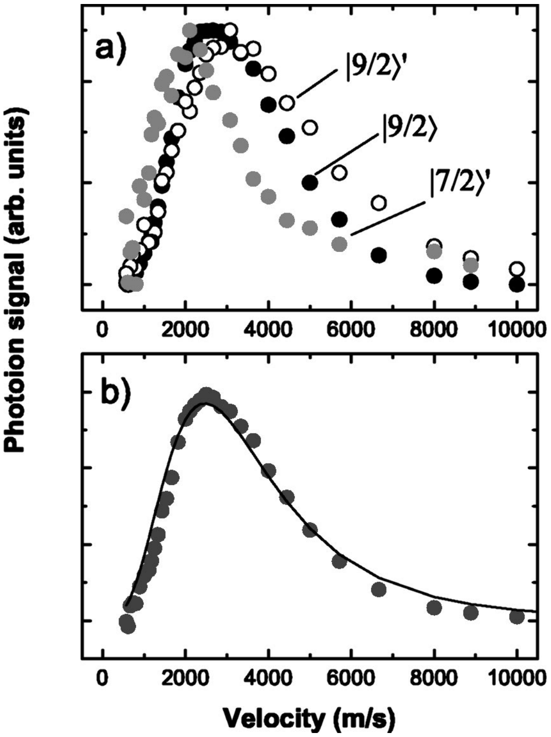

FIG. 4. Velocity distributions of sputtered Ir atoms. (a) Characteristic state-dependent velocity distributions. (b) Velocity distribution of the whole ensemble of detected sputtered neutral particles fitted by the Thompson distribution $f(v)$ (solid line) given in Eq. (1).

Ni atoms observed identical features [13,14]. We argued that these experimental observations could be interpreted as being the result of resonant electron transfer (RET) processes [15,16] between the bulk metal and the escaping particles [1,6,7], a conclusion also drawn in another investigation [14].

Here, we describe the key concepts of the resonant electron transfer process in the sputtering of neutral atoms in different atomic states. An elaborate description can be found elsewhere [6,7,14]. When the particles depart from the surface as a result of a collision cascade, they have to undergo electronic transitions. The metallic band levels, occupied by the electrons when the particles are inside the solid, are no longer accessible and the electrons have to evolve into atomic levels. After these transitions, most of the sputtered particles end up in neutral atomic states. The population probability for a sputtered particle to populate a specific fine structure state depends on several characteristics of both the atom and the metal.

First of all, the excitation energy of the atomic levels with respect to bulk metal properties such as the work function ϕ is important. A single-electron transition (which implies a resonant or energy-conserving transition) is favored above multielectron processes. Therefore the atomic levels must face occupied band levels in an energetic scheme as schematically presented in Fig. 5. As such, only atomic states with an excitation energy below $I-\phi$, in which I is the first ionization potential of the atom, will have a significant probability to become populated during the sputter process.

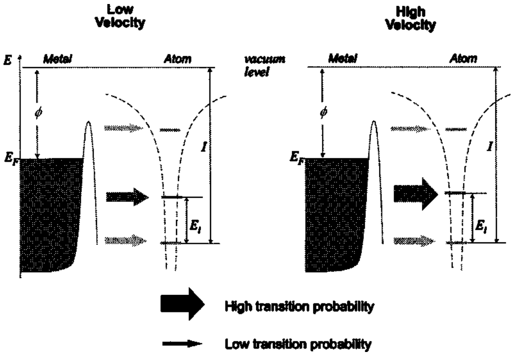

FIG. 5. Schematic representation of the most important features of the resonant electron transfer. If a particle is ejected with a very low velocity, all atomic states falling within the energy window determined by the metal valence band have a significant population probability. If a particle is ejected with a very high velocity, only transitions into atomic states with a bulk-type electron configuration have a significant probability.

Second, the electronic structure of both the atom and the metal plays a major role. The probability that an ejected particle ends up in a specific atomic state depends on the coupling between the atomic state and the metal electron levels. Atomic states with electronic wave functions that have a good overlap with those of the metal electrons will have a stronger coupling (the interaction matrix element is larger) and will be preferentially populated after the sputter event. Also the velocity of the escaping particle affects this state-dependent transition probability, as schematically presented in Fig. 5. For low velocities, the interaction time between the escaping particle and the bulk metal is long and consequently, the transition probability to all atomic states is still significant. If the particle is ejected with a high velocity, the interaction time is short and only a transition into an atomic state that is strongly coupled with the bulk metal levels has a significant probability. Therefore the population probability after sputtering on bulk-type atomic states will increase with increasing velocity of the ejected particles.

Whether the interpretation of the sputtering of atoms in different atomic states based on the qualitative features of the resonant electron transfer process presented above can also be applied to the sputtering of Ir atoms is investigated in the next paragraphs. The more complex electronic structure of Ir, due to strong configuration interaction, prohibits us to assign a single electron configuration to most of the atomic states of Ir. Instead, the atomic states of Ir must be expressed as expansions of pure *LS* states. These expansions were derived from a least-squares fit to the excitation energies of all known states with outer-shell electron configurations $5d^7\,6s^2$, $5d^8\,6s$, and $5d^9$ [8]. The results for the ground state and the six lowest-lying metastable states are listed in Table I. It is seen that even at low excitation energies strong deviations from pure *LS* coupling occur. The first excited state ($J=9/2$ and $E=0.35$ eV) is almost pure (96%) $5d^8\,6s\;b^4F_{9/2}$. Also for the ground state ($J=9/2$), the dominant contribution (84%) stems from a pure *LS* state ($5d^7\,6s^2\;a^4F_{9/2}$) and at the same time, the only other significant contribution also comes from an *LS* state with a $5d^7\,6s^2$ electron configuration. For

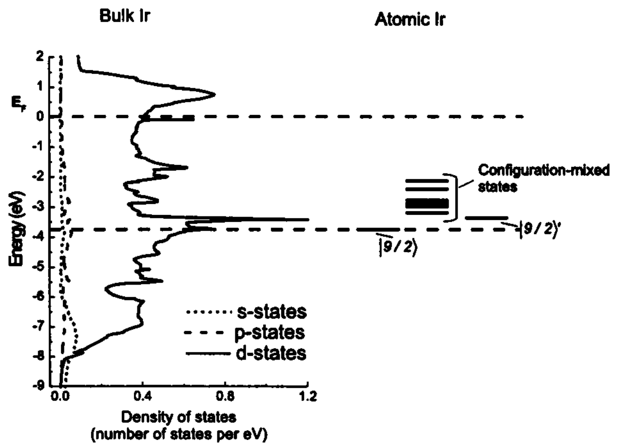

FIG. 6. The *s*-, *p*-, and *d*-density of states of metallic Ir near the Fermi level. On the same energy scale, the atomic states of Ir are drawn to the right. The region between the atomic ground state and the Fermi level E_F, bounded by the dashed, horizontal lines, is the energy window defined in the model describing the resonant electron transfer process.

all other involved states, the composition contains significant contributions of atomic states with different electron configuration. The composition of the atomic state $|7/2\rangle'$ is dominated by the contribution of the $5d^7\ 6s^2\ a^4F_{7/2}$ *LS* state, but note that the second highest contribution stems from an *LS* state with a $5d^8\ 6s$ electron configuration.

For the resonant electron transfer process, the interplay between the electronic structure of both the escaping atom and the bombarded metal is of major importance. Therefore an analysis of the electronic structure of metallic Ir is needed for a meaningful interpretation of our observations. To obtain information about the bulk electron configuration of Ir, the density of states of bulk Ir was calculated employing the WIEN97 program [17]. The results of these calculations are displayed in Fig. 6. The integrals of these density of states yield the bulk electron configuration, which is found to be [Xe] $4f^{14}\ 5d^{7.9}\ 6s^{0.6}\ 6p^{0.5}$. Noffke *et al.* reported a bulk electron configuration of [Xe] $4f^{14}\ 5d^{7.2}\ 6s^{0.7}\ 6p^1$ [18], which differs in the occupation of the hybridized *sp* orbital and the *d* orbital by almost one electron. The discrepancy is based on different assignments of the electrons in the interstitial space. But the main part of the density of states of the *s*-band lies around 7 eV below the Fermi energy. This is far below the energy window defined in the RET model. This means that the part of the valence band that the atomic states face while the atom is moving away from the metallic surface is more dominant in *d* character than the valence band as a whole. This effect is even more enhanced by the upward energy shift that the atomic states undergo in the vicinity of the metallic surface due to the image potential [15,16]. Therefore we can state that the part of the valence band faced by the atomic states during the sputter process is dominated by the *d* band.

The basic, qualitative features of the resonant electron transfer process outlined above can now be weighted against the experimental data, the population partition, and state-selective velocity distributions of sputtered Ir atoms. The work function of bulk Ir is 5.3 eV while the atomic ionization potential equals 9.0 eV. This implies that the atomic states of Ir with excitation energies up to 3.7 eV (see Fig. 5) are energetically in resonance with occupied valence-band states. Therefore the overall picture of the population partition shown in Fig. 3 agrees with a key element of the resonant electron transfer process during sputtering: all states within the energy window defined by the metal valence band will be substantially populated. Theoretical investigations of the resonant electron transfer process taking into account a single atomic state, yield that the population probability of that atomic level decreases with increasing energy difference between the atomic state and the Fermi level [15,16]. Under the (reasonable) assumption that this dependence survives a multilevel description, we can state that this effect corresponds with the overall decrease of the population on the atomic states of Ir with increasing excitation energy.

The state-selective velocity distributions indicate that we can classify the atomic states of Ir in three categories: (i) the ground state $|9/2\rangle$ of which the atoms have the highest average velocity, (ii) the first excited state $|9/2\rangle'$, and (iii) the other atomic states of which the atoms have the lowest average velocity. The difference between the velocity distributions of atoms sputtered in the ground state or in the first excited state can be interpreted within the framework of the resonant electron transfer process by taking into account the electronic structure of the atomic states. The first excited state $|9/2\rangle'$ is composed of *LS* states with a $5d^8\ 6s$ electron configuration while the ground state $|9/2\rangle$ is almost pure in the ^4F state with a $5d^7\ 6s^2$ electron configuration. As the bulk band structure is dominated by the *d* band, there is a close correspondence of the electron configuration of the first excited state with the relevant part of the valence band of the metal. Thus the first excited state has, in resonant electron transfer terms, a much stronger coupling with the metal states than the ground state. Consequently, the probability for a sputtered particle to end up in the first excited state increases with increasing ejection velocity, which explains the observed differences in the velocity distributions of the atoms sputtered in the ground state and the first excited state.

The other atomic states all contain significant contributions of *LS* states with a $5d^7\ 6s^2$ electron configuration as well as a $5d^8\ 6s$ electron configuration. Taking into account the large variations of the contributions in these “mixed” states, it is a peculiar observation that the velocity distributions of atoms sputtered in these states are identical within the experimental error. Furthermore, the velocity distributions of atoms in these states are narrow and peak at a much lower velocity than the velocity distribution of the ground state and the first excited state. A smaller average escape velocity for atoms in the excited states compared with atoms in the ground state was up to now only observed in sputtering investigations on Ag [19] and Cu [7]. Distributions that are skewed towards lower velocities indicate that the majority of the ejected particles remain longer in the vicinity of the surface. It already is well documented for the sputtering of ions that for longer interaction times between the metal and the departing particle other charge transfer processes gain importance [20,21]. From our experimental data, we can thus not exclude that other electronic processes substantially contribute to the population on the atomic states that are characterized by severe level mixing.

V. SUMMARY

We used doubled resonant laser ionization spectroscopy to study the sputtering of Ir particles in different atomic states after keV-ion beam bombardment of a pure Ir metal. The atomic states of Ir endure severe level mixing due to strong configuration interaction and as a result, only the ground state and the first excited state of Ir can be considered to be pure in a single electron configuration. All other involved states are mixtures of different *LS* states with different electron configurations.

We examined whether the observed population partition and state-selective velocity distributions are in agreement with the characteristics of the resonant electron transfer process. After sputtering, all probed states showed a significant population, which decreases with increasing excitation energy as predicted by the resonant electron transfer description. We also presented distinct differences in the velocity-dependent probability for a sputtered particle to populate a specific atomic state. The relative differences in the velocity distributions of atoms sputtered in the ground state and the first excited state, two states to which we can assign a single electron configuration, are well interpreted within the framework of resonant electron transfer processes by comparing the characteristics of the atomic levels with the calculated bulk metal levels. The velocity distributions of the other states, which are all mixtures of *LS* states with different electron configurations, are identical within the experimental uncertainty but shifted to lower velocities compared with the velocity distributions of the ground state and the first excited state. This observation cannot be interpreted in terms of the concepts of the basic RET model as presented above. Most likely, multiple electronic processes will contribute to the sputtering of particles in these mixed states.

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