The Electronic Excitation of Atoms in Atomization Processes Studied by Resonance Ionization Mass Spectrometry

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A laser ionization spectrometer designed for studying the atomization of metallic surfaces is presented. First experiments on polycrystalline nickel bombarded by 15 keV Ar^+ ions are reported. The sputtered neutral atoms are selectively excited and ionized using resonance ionization spectroscopy. A comparison is made between the two step-one colour and the two step-two colour schemes. The influence of autoionizing states on the ionization process is discussed.

1. Introduction

Atomization processes, i.e. the sputtering of neutral or charged atoms or clusters by the interaction of energetic beams of fast ions or laser photons with solid surfaces, are generally well documented both theoretically and experimentally [1,2]. More than 90% of the sputtered particles leave the target as neutral atoms, distributed over different excited states. The understanding of the mechanisms for the excitation of these atoms is still far from complete. Different models are proposed, but more experiments on well defined systems are needed.
A particularly well suited technique to probe the distribution of atoms over metastable states is provided by resonance ionization spectroscopy in combination with mass spectrometry (RIMS), due to its high elemental and state selectivity. With RIMS, the dependence of the population distribution over the different metastable excited states as function of different parameters involved, such as the matrix in which the atoms of interest are embedded, the environment in which sputtering takes place and the atomization process which is used, can be studied.
In this contribution we present our new RIMS apparatus designed for both laser and ion beam sputtering studies under UHV conditions. First experiments to determine the population distribution of ion beam sputtered Ni atoms from a polycrystalline Ni foil were carried out. It is shown that the sensitivity of the method is improved by resonance ionization into autoionizing states.

2. The Ionization Spectrometer

The Leuven RIMS-system is shown schematically in fig. 1. It consists of a spherical chamber equipped with a fast entry lock. The sample is mounted on a

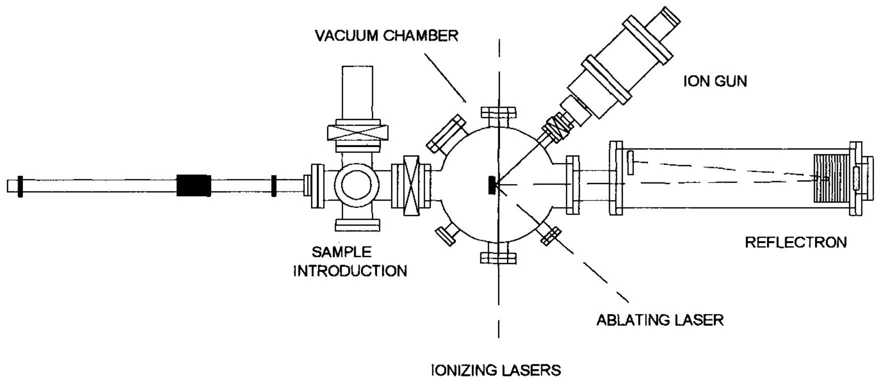

Fig. 1. Schematic top view of the recently built Leuven RIMS apparatus.

precision XYZΘ manipulator. The vacuum chamber is pumped by an ion getter pump and a titanium sublimator with a liquid nitrogen cooled cryoshield to provide a base pressure of less then 10^{-10} mbar free of organic contaminants. Particles can be atomized by laser evaporation and ion bombardment. The ion gun produces ion beams from inert or reactive gases, with an energy from 1 to 15 keV. Both primary beams hit the target under a 45° angle.

In the experiments described here, the sputtered particles are ionized with light from one or two pulsed Nd:YAG pumped dye lasers. Using DCM in methanol and frequency doubling in K*DP crystals, laserlight with wavelengths between 310 and 335 nm and linewidths of 0.1 cm^{-1} is available. The diameter of the ionizing laser beams is approximately 3 mm.

After ionization the particles are extracted electrostatically into a reflectron time-of-flight mass spectrometer and detected on dual microchannel plates. The voltage pulses are amplified and recorded by a fast digital oscilloscope. The mass resolution $m/\Delta m$ is about 500.

3. Experiments and discussion

Ni atoms are obtained after continuous bombardment of a 50μm thick polycrystalline Ni foil by a 15 keV Ar^+ beam (6 $\mu A/cm^2$). A laser beam with a pulse energy of 3.4 mJ, photoionizes the atoms resonantly via a two step-one colour proces. The spectrum obtained for ^{58}Ni (fig. 2a) shows that all metastable states up to the a^3P_1 level at 15734 cm^{-1} are significantly populated during the sputtering process. Some transitions starting from the different states are given in table 1 together with the observed line intensities.

Provided that the excitation and ionization steps are saturated, the relative population of two metastable states can be directly deduced from the relative amplitudes of the RIMS photo-ion signals. This condition is not always fulfilled in practice, as is illustrated in fig. 3, where the photo-ion signals as function of the pulse energy of the laser are shown for two ground state originating transitions:

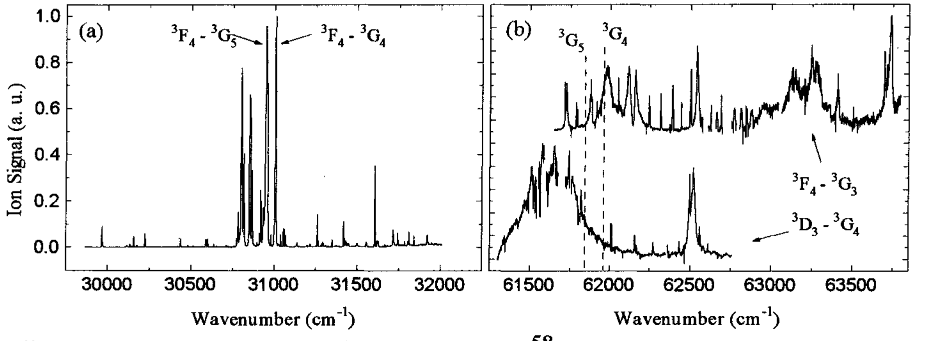

Fig. 2. (a) Two step-one colour ionization spectrum of ^{58}Ni and (b) Structure above the ionization potential.

$a^3F_4 \rightarrow z^3G_4$ (30980 cm^{-1}) and $a^3F_4 \rightarrow z^3G_5$ (30923 cm^{-1}). It is clearly seen that saturation is not reached for the ionization via the $^3G_5$ level.

In order to explain this difference in saturation behaviour, a two step-two colour scheme was used to study the continuum structure of Ni in more detail. The frequency of one laser was fixed to a resonant transition and the pulse energy was reduced untill the photo-ion yield from this ionization channel could not be distinguished from the background signal. By scanning the wavelength of the second laser at high pulse energy (3.4 mJ per pulse), different autoionizing states above the ionization potential (61619 cm^{-1} [4]) are observed. The obtained continuum structure for the transitions $a^3F_4 \rightarrow z^3G_3$ (31786 cm^{-1}) and $a^3D_3 \rightarrow z^3G_4$ (30775 cm^{-1}) is shown in fig. 2b. The wavenumbers at which the two ionization channels reach the continuum in the two step-*one* colour scheme, are indicated in the figure and illustrate that ionization via the $^3G_4$ level is enhanced due to the presence of an autoionizing state.

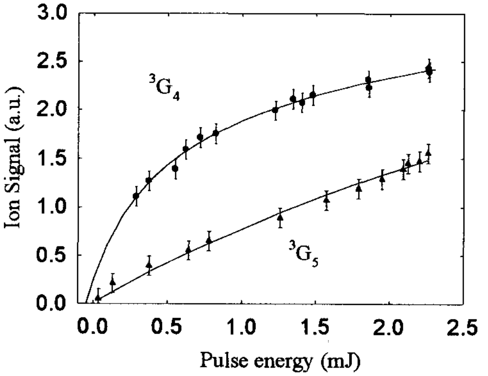

Fig. 3. Saturation behaviour of the ionization step of two groundstate originating transitions in the two step-one colour photo-ionization scheme [3].

The observed continuum spectrum also provides a clue for the explanation of several non-assigned lines in the one colour spectrum. Resonances are seen at exactly half the energy of the autoionizing states and could be interpreted as direct two-photon transitions to the continuum states. However, their angular momenta should be determined in order to make firm assignments.

For measuring population distributions, it is much more adequate to use a two step-two colour ionization

Table 1. Selected Ni transitions with relative intensities in the two-step-one colour photo-ionization scheme.

E_i (cm^{-1})	E_f (cm^{-1})	Transition	Rel. Int.
0	30980	$^3F_4 - {}^3G_4$	1.00
0	30923	$^3F_4 - {}^3G_5$	0.96
1332	31780	$^3F_3 - {}^3F_3$	0.03
2216	30766	$^3F_2 - {}^1P_1$	0.05
205	30826	$^3D_3 - {}^1F_3$	0.64
205	30775	$^3D_3 - {}^3G_4$	0.78
880	30906	$^3D_2 - {}^3G_3$	0.17
1713	31269	$^3D_1 - {}^1P_1$	0.02
3410	30999	$^1D_2 - {}^3D_1$	0.01
13521	30572	$^1D_2 - {}^5D_2$	0.04
15610	31529	$^3P_2 - {}^3D_2$	0.02
15734	31405	$^3P_1 - {}^3D_2$	0.03

scheme. In this case a minimal number of common intermediate states can be selected. The ionization step can then be optimized for maximum photo-ion yield by resonant transition to an autoionizing state. With the resonant excitation step being easily saturated, the obtained intensity of the photo-ion signal will always be proportional to the population of the metastable state. Since the energies of the metastable states differ by several eV, laser frequencies covering the full visible and UV spectrum are needed for the excitation step. For this purpose, we recently installed an optical parametric oscillator pumped by the third harmonic of a pulsed Nd:YAG laser, providing wavelengths between 440 and 1800 nm. Mixing and doubling further extends this range down to 220 nm.

Future experiments will concentrate on the study of the population distribution over the metastable states of nickel in different matrices with varying parameters of the sputterprocess.

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