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T. Gibert, P. Pezé, B. Dubreuil, M. Barthe, J. Debrun. MATERIAL ANALYSIS AND SURFACE INTERACTION STUDIES USING LASER RESONANT MULTIPHOTON IONIZATION. Journal de Physique IV Proceedings, 1991, 01 (C7), pp.C7-685-C7-688. 10.1051/jp4:19917184 . jpa-00250863

HAL Id: jpa-00250863

<https://hal.science/jpa-00250863>

Submitted on 1 Jan 1991

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MATERIAL ANALYSIS AND SURFACE INTERACTION STUDIES USING LASER RESONANT MULTIPHOTON IONIZATION

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Abstract - Resonance Ionization Spectroscopy (RIS) technique is an ultrasensitive method of detection of atoms and molecules. Application of RIS to material analysis requires an atomization step which is based in our set-up on ion beam sputtering. We present a review of the analytical studies we have performed demonstrating the very attractive potentialities of this method. RIS can be also used to study the surface sputtering process itself. Basic mechanisms of low energy laser desorption and vaporisation of metal samples have been investigated in this way.

I - Introduction

Resonant multiphoton ionization techniques using tunable pulsed dye lasers are widely used in the field of atomic and molecular spectroscopy /1/. By this method, known as "Resonance Ionization Spectroscopy" (RIS), atoms of a given element are selectively photoionized with a large probability. RIS is generally a two-step process in which atoms of the probed species are first excited in a well - defined quantum state by resonant absorption of n photons ($n=1,2$) of wavelength λ_1 and then photoionized by absorption of m supplementary photons ($m=1$ in most cases) of the same or of a different wavelength ($n + m$ photon process).

The first resonant step insures the elemental selectivity since only atoms in resonance are efficiently excited. This step saturates for $n = 1$ with relatively low laser power density. During this excitation stage, every excited atom can be further photoionized. The probability of this second step is much smaller than for the resonant step. However, using commercial tunable pulsed UV laser (with frequency doubling and mixing) of a few GHz bandwidth, (1+1) photoionization process can be saturated with only $10 - 100 \text{ MW/cm}^2$, whereas (2+1) photoionization process requires about 1 GW/cm^2 .

This is illustrated below (Fig. 1) in the case of (1+1) photon ionization of Mg ($\lambda = 285.2 \text{ nm}$) and Fe ($\lambda = 293.7 \text{ nm}$) /2/ respectively and of the (2+1) photon ionization of P ($\lambda = 299.3 \text{ nm}$) /3/. These atoms were produced by ion sputtering of solid samples in a ultra-high vacuum chamber.

Fig. 1 - Resonant multiphoton ionization yield of Mg, Fe and P atoms as a function of the laser power density.

II - Trace analysis in materials using RIS and ion beam sputtering

Good selectivity, near unity photoionization yield make RIS very attractive for elemental analysis. Trace analysis in materials requires an atomisation step before RIS is applicable. The aim of this step is the liberation of neutral atoms representative of the atomic composition of the sample. Among different atomization methods, ion beam sputtering appears particularly well adapted, allowing lateral resolution in the micrometer range, depth profiling and precise control of the material consumption. Furthermore, in the case of metals and semiconductors most of the sputtered particles are neutral atoms (non reactive sputtering). With insulators or with reactive sputtering the amount of secondary ions can reach a few tens of percent.

In our laboratory, coupling of RIS with ion beam sputtering technique (SIRIS : sputtered initiated RIS /4/) is developed around a U.H.V. chamber, a Ar^+ duoplasmatron ion gun, a quadrupolar mass - spectrometer and a Nd : Yag laser pumped dye laser with doubling and mixing.

Due to the pulsed operation of the probe laser beam, two modes of analyses are possible. In c.w. sputtering, the ion beam continuously sputters the surface whereas the laser beam periodically (10 Hz) probes the concentration of a given species at increasing depths in the material (depth profiling). In pulsed operation, the ion beam sputters the surface during a short time (1 - 10 μs), producing a cloud of atoms propagating perpendicularly above the surface. The probe laser is fired at the time when the expanding packet crosses the interaction zone. The sputtering duration is adjusted for the best overlap between the atom cloud and the laser beam. In this mode, the material consumption is very small.

Advantages of SIRIS over other surface analytical methods (SIMS) are :

- elimination of matrix effects in metal and semiconductors /5/
- linearity and quantitativity /5/
- high sensitivity, large useful yield : 1 ppm detection on a single laser shot for a (1+1) photon process with the sputtering of less than a monolayer /2/, 100 ppm for a (2+1) photon process /3/.
- removal of mass-interferences /3/.
- pulsed operation for analysis of insulating materials (minimizes

charging effects and field effects on the surface).

For example, Fig. 2 shows the recording in counting mode (2000 laser shots) of the Fe^+ photoion pulse obtained from a 13 ppm Fe doped SiO_2 sample. In this experience, pulsed sputtering conditions were used to overcome the problem of charging effects /6/. Note also the efficient discrimination between ^{56}Fe photoions and $^{28}\text{Si}_2$ secondary ions - a typical mass - interference problem.

Fig. 2 Detection of 13 ppm of Fe in SiO_2 : recording of the Fe^+ photoion pulse corresponding to 2000 laser shots in pulsed sputtering conditions. Material consumption : less than a monolayer on a 300 μm diameter spot.

III - RIS studies of ion or laser beam interaction with surfaces

Several surface characterization methods as well as material processing techniques (film deposition, etching, surface treatment ...) are based on the interaction of energetic beams of particles or laser beams with materials. One can get an insight into the physics of the interaction process by analysing the characteristics of the particles which are emitted by or scattered from the surface. For example, using RIS, Winograd et al. /7/ made an energy and angle resolved analysis of atoms sputtered from a surface by an incident Ar^+ ion beam and compared the results with sophisticated models describing the collision processes between incident ions and atoms of the material.

In the case of film deposition using either ion beam or laser beam sputtering of a composite material, real - time monitoring and precise control of the process needs knowledge of the space and energy distributions of the sputtered products as well as their chemical composition as they impinge on the substrate. Since most of these processes are performed under vacuum or very low pressure conditions, RIS is relatively well adapted for this purpose. Using the SIRIS experimental set-up, we have measured the relative concentrations of oxygen and copper atoms which are emitted during the Ar^+ ion beam sputtering of a YBaCuO superconducting target. A very low emission of oxygen atoms was detected in agreement with other observations /8/, indicating that most of the oxygen of the material is sputtered as metal oxides.

Surface sputtering induced by an incident laser beam (ablation, vaporization) is also becoming increasingly important as technologies are

developed which utilize this process. Basic mechanisms of low energy laser desorption and vaporization are currently under study in several groups /9, 10/. We have investigated using RIMS, the sputtering of iron and alloys surfaces irradiated by the focused beam of a N₂ laser in the 20 - 350 mJ/cm² fluence range.

Delaying the RIS probe laser beam with respect to the ablating laser pulse, the time-of-flight (TOF) distribution of Fe atoms emitted by the irradiated surface was recorded as a function of the incident laser energy. Fig. 3 shows such TOF distribution obtained for a 120 mJ/cm² fluence. These distributions are compared to theoretical models : pure thermal emission (half-space Maxwell distribution) or hydrodynamical model (Maxwell distribution with a finite center of mass velocity). In the laser fluence range investigated, it appears that pure thermal emission model fits rather well our experimental results as the density of emitted atoms is too low to establish a Knudsen layer on the surface. The kinetic temperature of the atomic beam is directly deduced from the fits.

Atomic excitation temperature is determined from RIS probing of the population distribution in the fine structure levels of the Fe ground state. The results are reported in Fig. 4 as a function of the laser fluence and are compared with the kinetic temperature. The reasonable agreement which is observed, corroborates the pure thermal model. It is interesting to note that in this case the excitation temperature probed in the atomic beam reflects rather well the thermal state of the atoms as they leave the surface. Indeed one observes in Fig. 4 an increase of the excitation temperature from the ambient at the threshold to the melting and boiling temperature values at the highest laser energies.

Fig. 3 - T.O.F. distribution of Fe atoms emitted by a alloy sample irradiated by the beam of a N₂ laser

Fig. 4 - Excitation and kinetic temperatures of the evaporated Fe atoms

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