Appl. Phys. A 52, 213–217 (1991)

Applied Physics A Solids and Surfaces

Cluster Emission under Ion Bombardment of Metallic Targets

P.Wurz, W. Husinsky, and G. Betz

Institut für allgemeine Physik, Technische Universität,
Wiedner Hauptstrasse 8–10/134, A-1040 Wien, Austria

Received 9 February 1990

Abstract. Mass spectroscopic studies of the neutral particles sputtered by Ar^+ ions at 8 keV from polycrystaline samples have been performed, using non-resonant laser ionization and subsequent time-of-flight mass spectroscopy. Besides sputtered atoms, also dimer and trimer contributions in the order of 10^{-1} to 10^{-2} and 10^{-3} to 10^{-4}, respectively, are found in the sputtered flux. The data obtained here together with previously published data by other groups for different bombarding energies provide strong support for the validity of the recombination model.

PACS: 36.40

If a clean metal is bombarded with inert gas ions, it is well known that the sputtered flux consist mainly of neutral monoatomic target particles. Only a small fraction of the sputtered flux are molecules, namely dimers and trimers. Cluster emission has attracted attention from experimebntalist [1-6] as well as theoreticians [7, 8] but the formation mechanism is still not generally agreed on. Besides a pure scientific interest in the cluster formation mechanism, sometimes sizable contributions of clusters to the total yield have to be taken into account when using sputtered neutrals for quantitative analysis. As a general trend, the amount of dimers and trimers was found to be several percent and several permil, respectively, compared to the amount of sputtered atoms [7]. Although a considerable amount of experimental data appear in the literature on the sputtering of ion clusters, data on neutral clusters are scarce. In addition, the measured neutral cluster yields differ substantially. In particular, cluster yields reported in [4] are significantly higher than reported in other works.

Basically, two different models for the formation of clusters have been proposed. Originally it was thought that clusters leave the surface as an entity, that is, the cluster constituents are nearest neighbors before the ejection event and leave the surface after one of the constituents of the molecule has encountered a single collision [9]. This mechanism will be operative if the intramolecular binding is strong compared to the intermolecular or surface binding of the whole molecule (e.g., adsorbates on surfaces). The atoms which will form the cluster are independently ejected from the surface by different recoils. A stable cluster will develop if their relative kinetic energy is less than the binding energy of the cluster at their distance of closest approach. The atoms of the clusters can either be bound prior to emission or recombine after the sputter event. This situation usually applies for cluster emission from clean metals. A recent review of the different concepts can be found, for example, in [11, 12]. One way to distinguish between the two models is to measure the kinetic and ro-vibrational energy distribution. In the case of the single collision mechanism, a characteristic cut-off in the energy distribution at the dissociation energy should exist. In the case of the recombination mechanism, a characteristic experimentally detectable feature is the pronounced population of higher ro-vibrational states [13].

The recombination mechanism predicts that the yield of clusters containing n atoms, Y_n, should increase with the nth power of the total sputter yield

S of the sample,

$$Y_n = k_n S^n , \quad (1)$$

where $n \leq 3$ [7].

Computer simulations show that multiple interaction of particles in the near-surface region may indeed lead to the formation of clusters from atoms which originate within a circular region of roughly 70 Å^2 or less, not necessarily centered around the impact of the primary ion [14] and not bound before. Unfortunately, these simulations cannot reproduce the dependence of the cluster yield Y_n upon the energy, respectively sputter yield S [15].

The ambition to investigate the sputtered neutral clusters encounters the experimental problem to efficiently postionize the particles after removal from the sample surface for subsequent mass analysis. This technique is called Secondary Neutral Mass Spectroscopy (SNMS), which requires more experimental efforts than the detection of sputtered cluster ions using the established Secondary Ion Mass Spectroscopy (SIMS) [16]. Postionization can be achieved by electron-impact ionization [17], by passing a gas discharge [18], or by non-resonant multiphoton ionization [19]. For mass analysis, sector magnets, quadrupol and time-of-flight mass spectrometers are used. Each postionization scheme has different ionization cross-sections. In this paper we will compare results on the sputtering of clusters using the rather new method of multiphoton ionization with the results obtained with other techniques.

Experimental

The experiments were performed under UHV conditions ($2 \cdot 10^{-10}$mbar base pressure) using a newly developed SNMS/SIMS instrument, which is shown in Fig.1. More detailed information of the instrument can be found in [20]. In this device Time-of-Flight (ToF) mass spectrometry can be performed with either photoionized sputtered/desorbed neutral atoms and molecules by intense laser radiation, or direct analysis of the secondary ions. In the SNMS-mode the atoms and molecules sputtered by the probe beam are ionized by nonresonant laser multiphoton ionization (MPI) [21,22]. The photoions are accelerated into a high resolution ($m/\Delta m = 1000$), high transmission ToF mass spectrometer of the reflecting type [23] and detected by a chevron microchannel plate assembly. In this mode the detection efficiency is $\simeq 10^{-3}$. Any secondary ions formed are electrostatically suppressed in SNMS mode [20]. ToF mass spectrometry has the big advantage that all masses are recorded quasi-simultaneous. A Lambda Physik excimer laser operated with XeCl (wavelength: 308nm) was used for photo ionization. The analysis was performed with a 8 keV Ar$^+$ beam with up to 2 μA current and a beam diameter of 3 mm provided from a Colutron ion source. The ion gun axis was tilted 45° from the target normal.

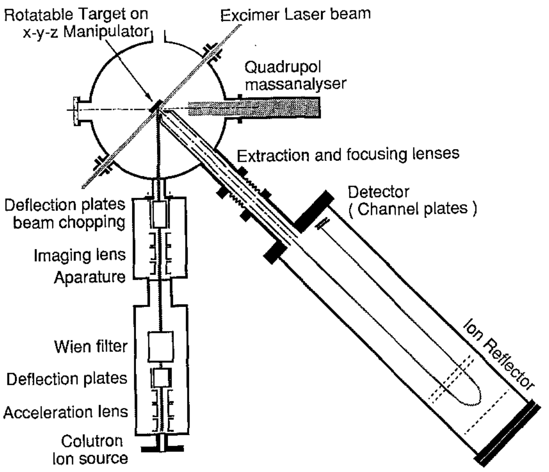

Fig.1. Schematics of the experimental apparatus

Results and Discussion

Sputtering of atom- and multimer-emission under Ar$^+$ bombardment from pure Al, Cu and Ta samples, as well as Cu and Ag from an alloy sample ($Ag_{0.4}Au_{0.4}Cu_{0.3}$) has been investigated. Figure 2 shows a typical mass spectrum from sputtered neutrals from an $Ag_{0.4}Au_{0.4}Cu_{0.3}$ alloy under 8 keV Ar$^+$ bombardment. In addition to atoms, even complex clusters are easily identified by their natural isotopic abundance. In all cases atoms, dimers and sometimes trimers are found.

Our experimental results for the relative sputter yields of dimers and trimers are summarized in Table 1, together with available data from the literature. These results support the present understanding that for most materials the amount of dimers and trimers is several percent and several permil, respectively, compared to the amount of sputtered atoms. Notable exceptions to these rules are Ag and Cu, where the yield of sputtered clusters is more pronounced. Furthermore, it is noticed that values reported in [4] are, in general, higher than those reported by other researchers.

The measurements for Cu under Ar$^+$ bombardment from Table 1 for different primary energies are plotted versus the sputter yield [24] in Fig.3 (in the energy range from 90eV to8 keV). An energy dependence has also been measured in single experiments, in the range of 50 to 90 eV by [6] to 300 eV by [4] and 100 to 1000 eV by [2] and these results

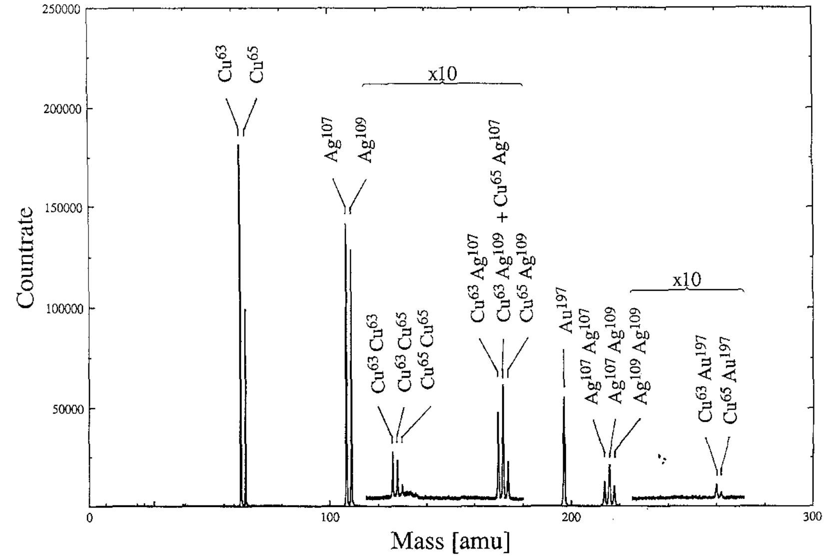

Fig.2. A typical mass spectrum recorded with 8 keV Ar^+ bombardment of $Ag_{0.4}Au_{0.4}Cu_{0.3}$

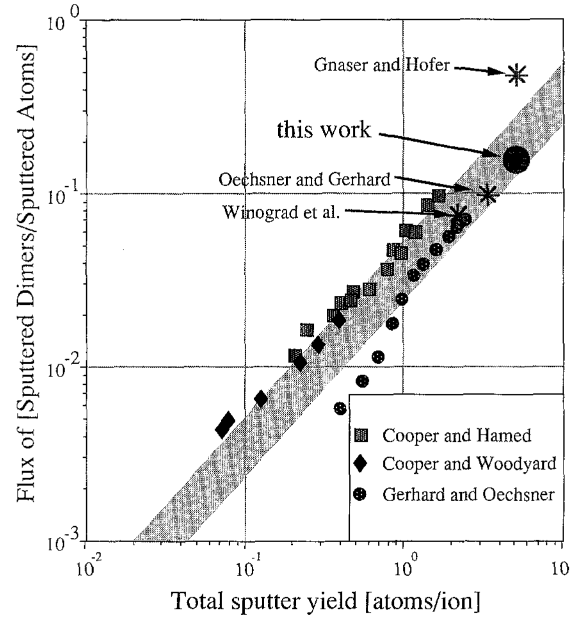

Fig.3. The ratio of sputtered dimers to sputtered atoms vs the sputter yield is shown for Cu. Data points are from Table 1, from [6] in the energy range from 50 to 90 eV, from [4] in the energy range from 100 to 1000 eV, and [2] in the energy range from 60 to 300 eV. A linear fit through the data points is indicated

are added in Fig.3. Note that different experimental approaches have been used to obtain the data [1-6]. Assuming the validity of (1) and herewith the recombination model, plotting Y_2/Y_1 versus S should result in a linear dependence if most of the particles are sputtered as atoms. Indeed, a satisfactory linear relationship can be found, although there is some scatter between data from different researchers, which results in different values for k_2. Data from [2] deviates from the linear relationship for low primary energies. Also, a recently published result [4] seems to exceed the expected linear dependence.

The factor k_2 should not be considered a general constant for the sputtering of dimers, because it incorporates stability criteria of the molecule like the dissociation energy and also the ionization energy. In addition, a transmission of the instrument which decreases for higher masses also lowers k_2. Therefore k_2 should change from species to species rather than remain constant for different materials as emphasized in [2].

An energy dependence has also been measured for Ag in the range of 100 to 1000 eV [2]. Again, the linear relation between the ratio Y_2/Y_1 and the sputter yield is found only above a certain energy in this measurement in the same way as for Cu (Fig.3). Our result for Ag is also found on the linear fit of the data points from [2].

It is interesting to compare the sputter yield of dimers from a pure metallic sample with the alloy. If the dimer sputter yield of Cu from the sample is corrected for the stoichiometry of the alloy, almost the same value as for pure Cu is found. This is striking evidence of the validity of the recombination mechanism because, due to stoichiometry, a fraction of the clusters found could not be nearest neighbors before ejection from the surface.

For comparing different values in Table 1, the different experimental methods and their consequences for measuring sputter yields of clusters have to be discussed in some detail. In particular the following three issues have to be considered:

a) Ionization probability of the particular ionization method,
b) fragmentation of molecules,
c) mass dependent transmission of the instrument.

In the case of MPI, saturation of the photo-ion signal is achieved, as verified experimentally (all neutral particles in the interaction volume are ionized). With the other post-ionization techniques on-

Table 1. Compilation of available ratios Y_2/Y_1 and Y_3/Y_1 with experimental conditions and techniques. Data marked with * are corrected for stoichiometry of the sample. (Mat.: metal, here: this paper, im.: impact)

Met.	M_2/M	M_3/M	Ref.	Experimental	Postionizat.
Al	$1.89\cdot10^{-2}$	-	here	8keV $Ar^+\rightarrow Al$	MPI
Ti	$6.6\cdot10^{-3}$	$5.7\cdot10^{-4}$	[4]	5keV $Ar^+\rightarrow Ti$	Electron im.
V	$3.4\cdot10^{-2}$	$4.4\cdot10^{-4}$	[4]	5keV $Ar^+\rightarrow V$	Electron im.
Cr	$2.0\cdot10^{-2}$	$1.05\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Cr$	Electron im.
Fe	$2.8\cdot10^{-2}$	$1.7\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Fe(110)$	Electron im.
Ni	$5.2\cdot10^{-2}$	$5\cdot10^{-4}$	[5]	1keV $Ar^+\rightarrow Ni$	HF-Plasma
Ni	$4.25\cdot10^{-2}$	-	[2]	1keV $Ar^+\rightarrow Ni$	HF-Plasma
Ni	$20\cdot10^{-2}$	-	[4]	5keV $Ar^+\rightarrow Ni$	Electron im.
Ni	18.10^{-2}	$10\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Ni(111)$	Electron im.
Cu	$1.9\cdot10^{-2}$	-	[6]	90eV $Ar^+\rightarrow Cu$	Plasma
Cu	$4.6\cdot10^{-2}$	-	[3]	200eV $Ar^+\rightarrow Cu$	Plasma
Cu	$7.3\cdot10^{-2}$	$9.3\cdot10^{-3}$	[14]	600eV $Ar^+\rightarrow Cu$	Simulation
Cu	$10.4\cdot10^{-2}$	$1\cdot10^{-3}$	[5]	1keV $Ar^+\rightarrow Cu$	HF-Plasma
Cu	$7.7\cdot10^{-2}$	$6.7\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Cu$	HF-Plasma
Cu	$43\cdot10^{-2}$	$14\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Cu$	Electron im.
Cu	$42\cdot10^{-2}$	$14\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Cu(111)$	Electron im.
Cu	$18.6\cdot10^{-2}$	-	here	8keV $Ar^+\rightarrow Cu$	MPI
Cu*	$16.5\cdot10^{-2}$	-	here	8keV $Ar^+\rightarrow AgAuCu$	MPI
Ge	$14\cdot10^{-2}$	$40\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Ge$	Electron im.
Ge	$14\cdot10^{-2}$	$37\cdot10^{-3}$	[4]	5keV $Ar^+\rightarrow Ge(111)$	Electron im.
Zr	$1.6\cdot10^{-2}$	$11.7\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Zr$	HF-Plasma
Mo	$3.0\cdot10^{-2}$	1.10^{-4}	[2]	1keV $Ar^+\rightarrow Mo$	HF-Plasma
Mo	$2.2\cdot10^{-3}$	$4\cdot10^{-6}$	[1]	4keV $Ar^+\rightarrow Mo$	MPI
Pd	$3.2\cdot10^{-2}$	10^{-4}	[2]	1keV $Ar^+\rightarrow Pd$	HF-Plasma
Ag	$10.3\cdot10^{-2}$	$14.6\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Ag$	HF-Plasma
Ag*	$33\cdot10^{-2}$	-	here	8keV $Ar^+\rightarrow AgAuCu$	MPI
Hf	$1.15\cdot10^{-2}$	$2.7\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Hf$	HF-Plasma
Ta	$2.2\cdot10^{-2}$	$15\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Ta$	HF-Plasma
Ta	$4.76\cdot10^{-3}$	$8.62\cdot10^{-4}$	here	8keV $Ar^+\rightarrow Ta$	MPI
W	$2.9\cdot10^{-2}$	$10.7\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow W$	HF-Plasma
Pt	$4.2\cdot10^{-2}$	$11.9\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Pt$	HF-Plasma
Au	$12.2\cdot10^{-2}$	$15.8\cdot10^{-4}$	[2]	1keV $Ar^+\rightarrow Au$	HF-Plasma

ly a fraction of the sputtered flux is ionized, depending on the ionization cross section which changes from species and, in particular, from atoms to clusters. For electron-impact ionization an ionization factor of 10^{-4}, for plasma ionization 10^{-2} is achieved [2]. Limitations in the quantitative analysis of the latter two methods are expected from this side.

Fragmentation during the ionization process is a general problem in SNMS. For electron impact ionization this phenomenon is well understood, due to the widespread use of quadrupol mass spectrometers. Fragmentation also occurs in a plasma discharge and the reader is referred to [2] for a detailed discussion. In the case of multiphoton ionization of neutral molecules, fragmentation due to the intense laser field can occur. By changing the laser intensity, we are able to observe saturation of each signal and also, for high laser intensities, fragmentation of molecules. With this knowledge, the laser power is set as high as necessary to saturate the signals and also to avoid fragmentation. Unfortunately, saturation of atoms takes more power than saturation of molecules, due to the lower ionization potential of molecules. Thus fragmentation can already occur below saturation of the molecular signal, depending on the dissociation compared to the ionization energy of the molecule. Actually, the ionization probability in a multi-photon process is much more complicated and involves intermediate atomic levels as well as the laser wavelength [21,22]. Also resonant excitation of an antibonding state of the molecule can suffice to fragment the molecule of interest. Summarizing all this, a detailed statement about fragmentation of a particular molecule can only be given after a careful study of the diatomic potentials curves with respect to laser wavelength and selection rules. Additional information on fragmentation can be obtained by changing the laser wavelength and thus avoiding resonant dissociation. Another possibility would be to use laser-photons with very high energy (≥10eV), so that every molecule can be ionized by absorbing only a single photon, thus only moderate laser intensities are necessary [25].

Mass dependence of the transmission of the instrument seems only to be a problem for quadrupol mass spectrometers, where the transmission decreases with increasing mass. However, in [2,5] it was claimed that work is done in a mode where the transmission is constant over the mass range of interest.

Conclusions

We presented new data on the cluster formation by sputtering of metals using the technique of MPI and time-of-flight mass spectroscopy. The results agree well with similar measurements performed with other techniques. Summing up the compiled experimental data, there is good agreement about the magnitude of the yield of sputtered clusters, namely the amount of dimers and trimers is several percent and several permil, respectively, compared to the amount of sputtered atoms. This, together with the linear dependence of Y_2/Y_1 on the sputter yield, supports the validity of the recombination mechanism. For high sputter yields, S limitation of the ratio Y_2/Y_1 is expected when the flux of dimers becomes comparable to the flux of atoms, but is not observed in experiment. The measurements on the alloy give additional support for the recombination model. The only exceptions to the general rule is Cu and Ag, which have higher sputter yields for clusters.

Acknowledgements. The financial support of the "Österreichischen Fonds zur Förderung der wissenschaftlichen Forschung" (project number: P 6386 Phy) is gratefully acknowledged.

References

1 M.J. Pellin, W. Husinsky, W.F. Callaway, J.W. Burnett, E.L. Schweitzer, C.E. Young, B. Jorgensen, D.M. Gruen: J. Vac. Sci. Technol. B 5, 1477 (1987)
2 W. Gerhard, H. Oechsner: Z. Physik B 22, 41 (1975)
3 C.B. Cooper, H.A. Hamed: Surf. Sci. **143**, 215 (1984)
4 H. Gnaser, W.O. Hofer: Appl. Phys. A **48**, 261 (1989)
5 H. Oechsner, W. Gerhard: Surf. Sci. **44**, 480 (1974)
6 C.B. Cooper, J.R. Woodyard: Phys. Lett. A **79**, 124 (1989)
7 W. Gerhard: Z. Physik B 22, 31 (1975)
8 G.P. Können, A. Tip, A.E. deVries: Rad. Eff. **21**, 269 (1974)
9 A. Benninghoven, A. Müller: Surf. Sci. **39**, 416 (1973)
10 G.P. Können, A. Tip, A.E. deVries: Rad. Eff. **26**, 23 (1975)
11 H.M. Urbassek: Nucl. Instr. Meth. B **18**, 587 (1987)
12 H.M. Urbassek: Nucl. Instr. Meth. B **31**, 541 (1988)
13 K. Snowdon, R. Hentschke, W. Heiland, P. Hertel: Z. Physik A **318**, 261 (1984)
14 N. Winograd, D.E. Harrison Jr., B.J. Garrison: Surf. Sci. **78**, 467 (1978)
15 N. Winograd, K.E. Foley, B.J. Garrison, D.E. Harrison Jr.: Phys. Lett. A **73**, 253 (1979)
16 A. Benninghoven, F.G. Rüdenauer, H.W. Werner: *Secondary Ion Mass Spectroscopy* (Wiley-Interscience, London1987)
17 R.E. Honig: J. Appl. Phys. **29**, 549 (1958)
18 H. Oechsner: in, *Thin Solids and Depth Profile Analysis*, ed. by H. Oechsner, Topics Curr. Phys. **37** (Springer, Berlin, Heidelberg 1984) p.63
19 C.H. Becker, K.T. Gillen: Anal. Chem. **56**, 1671 (1984)
20 P. Wurz: Dissertation (1990)
21 P. Lambropoulos: Adv. At. Mol. Phys. **12**, 87 (1976)
22 J. Morellec, D. Normand, G. Petite: Adv. At. Mol. Phys. **18**, 97 (1982)
23 B.A. Mamyrin, V.I. Karataev, D.V. Shimkk, V.A. Zagulin: Sov. Phys. JETP **37**, 45 (1973) (English translation)
24 N. Matsumani, Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, R. Shimizu, H. Tawara: Inst. Plasma Physics, Nagoya University, **IPPJ-AM-32** (1983)
25 J.B. Pallix, U. Schüle, C.H. Becker, D.L. Huestis: Anal. Chem. **61**, 806 (1989)