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Sputtering of clean and oxidized Cr and Ta Metal Targets using SNMS and SIMS.

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Introduction

Metal and metal oxides are materials, which are important for many applications. Therefore, reliable quantitative analysis methods for oxides are desired. If a clean metal is bombarded with rare gas ions, it is well known that the sputtered flux consist mainly of neutral monoatomic target particles. However the composition of the sputtered flux changes drastically if the surface is partially or fully oxidized.

It is well known from secondary ion mass spectroscopy (SIMS) [1] and from bombardment induced light emission (BLE) measurements [2], that the yield of ions as well as excited neutrals increases by orders of magnitude with increasing oxygen coverage of the surface. On the other hand, it is especially this effect which is used in SIMS to enhance the sensitivity. The strong matrix effects in the generation of secondary ions and excited atoms are a serious limitation for these techniques for quantitative surface analysis. To overcome this problem analysis of sputtered neutral atoms has been proposed for better quantitative surface analysis. In short, the approaches can be clasified in probing a particular atom in a particular state (laser induced fluorescence, LIF) or ionizing and mass-analyzing the neutral sputtered flux without regard for excitation of a sputtered particle (secondary neutral mass spectroscopy, SNMS). Postionization in SNMS, can be achieved by electron impact ionization [3], by an Ar-plasma [4], by resonant multiphoton ionization [5] or by non-resonant multiphoton ionization [6]. Analysis of sputtered neutral atoms may also suffer from matrix effects, due to the chemical environment on the sample surface. In general, a decrease of the yield of neutral metal atoms sputtered from oxidized surfaces compared to clean metals have been observed, although LIF [7-9] and SNMS [4,10] investigations disagree considerably about the magnitude of the effect. This may be partly due to inherent experimental aspects of the different techniques, but the presence of matrix effects seems to be well established. A recent summary on this topic can be found in [11]. In the present paper we compare SNMS and SIMS measurements of gradually oxidized surfaces, performed under identical experimental conditions.

Experimental

The experiments were performed under UHV conditions ($2\cdot10^{-10}$mbar base pressure) using a newly developed SNMS/SIMS instrument. Details of the instrument can be found in [12]. This device employs time-of-flight mass spectrometry of either photoionized sputtered/desorbed neutral atoms and molecules by intense laser radiation, or direct analysis of the secondary ions. Time-of-flight mass spectrometry has the big advantage that all masses are recorded quasi-simultaneous. A Lambda Physik excimer laser operated with XeCl (wavelength of 308nm) was used for photo ionization. The analysis was performed with a 8keV Ar^+ beam with up to 2μA dc current and a beam diameter of 3mm provided from a Colutron ion source. The ion gun axis is tilted 45° from the target normal. Oxygen is introduced to the sample through a tube from an inlet valve, directed under 60° from the surface normal releasing the gas at a distance of 8mm.

In SNMS-mode the atoms and molecules sputtered by the Ar^+ beam are ionized by nonresonant multiphoton ionization (MPI)[13,14]. The photoions or secondary ions are accelerated into a high resolution ($m/\Delta m=1000$), high transmission time-of-flight mass spectrometer of the reflecting type [15] and detected by a chevron microchannel plate assembly. In this mode the detection efficiency is $\approx 10^{-3}$. Any secondary ions formed are electrostatically supressed in SNMS mode [12].

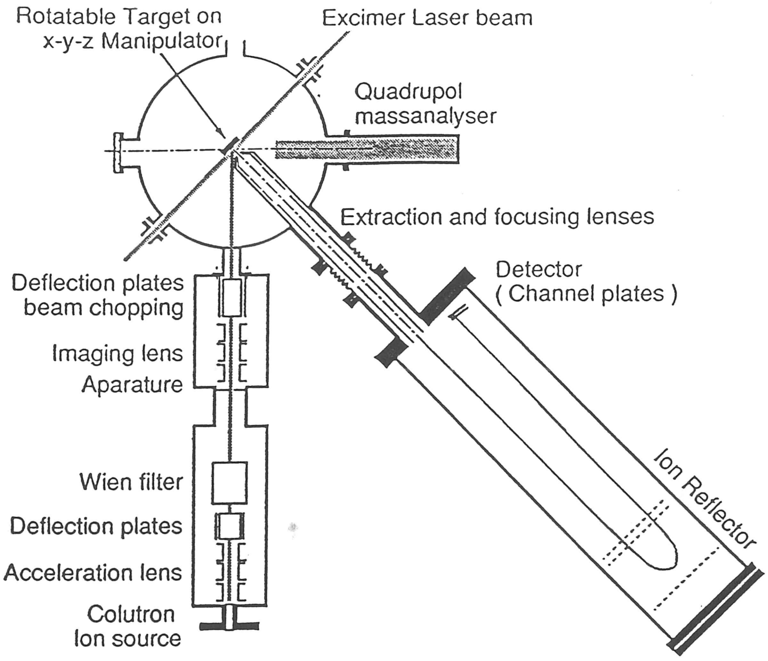

Figure 1: SNMS and SIMS ToF spectrometer.

For SNMS two modes of operation are possible: a) Constant primary current (dynamic mode); b) Pulsed primary current with ion on for pulses of $\approx 10\mu sec$ with the laser fired at the end of each pulse (static mode). In static mode very little surface damage is caused by the primary ion beam. The flux of primary ions in this mode is $9.2 \cdot 10^{10}$ions/sec·cm^2. In dynamic mode, not only high erosion of the sample, but also implantation of oxygen into the sample takes place, thus surface composition reflects the interplay of Ar ion bombardment and oxygen exposure.

In SIMS-mode the measurements only are performed in the static regime due to the nature of the instrument. The detection efficiency is a factor of 10 higher than in SNMS mode. The flux of primary ions in SIMS mode is $4.2 \cdot 10^9$ions/sec·cm^2.

Results

For static conditions, the dependence of the yields of neutral Cr and CrO on the oxidation of the surface as obtained by SNMS is shown in fig. 2. The Cr signal does not seem to be affected by the oxygen concenctration as it stays almost constant over the full range of oxygen flux. The only sputtered neutral molecule observed is CrO. Its signal is smaller by a factor of 6.5 than the Cr signal for fully oxidized surface. Comparing static and dynamic modes the presence of CrO_2 in case of the dynamic mode might indicate that implantation and mixing of oxygen in the uppermost atomic layers of the metal is effective.

Figure 3 shows the SIMS measurement of Cr sample under oxygen coverage. The Cr^+ secondary ion yield increases from the clean to the fully oxidized surface by a factor of 190. A saturation in the Cr^+ yield is found above a rate of $2 \cdot 10^{12}$oxygen molecules/sec·cm^2. Oxide ions (CrO and CrO_2), which are not present on a clean surface appear at a flux of $3 \cdot 10^{11}$oxygen molecules/sec.cm^2. Worth mentioning is the $Cr_2{}^+$ dimer, which is not sputtered from the clean surface, but is detected with increasing oxidation of the surfaces. At high fluxes of oxygen molecules, the Cr_2 dimer disappears again. The total Cr^+ yield is smaller by a factor of 0.07 than the total neutal Cr yield for oxidized surface. The magnitude of increase and saturation of the Cr^+ secondary ion yield agrees well with a previous measurement [16], performed also under static conditions. In [16], an increase by a factor of 240 and saturation of the Cr^+ yield above an exposure of 500L oxygen (static exposure) was found.

In case of sputtering Ta metal we not only see Ta atoms and clusters but also TaO and TaO_2 in the SNMS spectrum shown in fig. 4, even for a clean surface. The ratio of the signals of metal clusters to

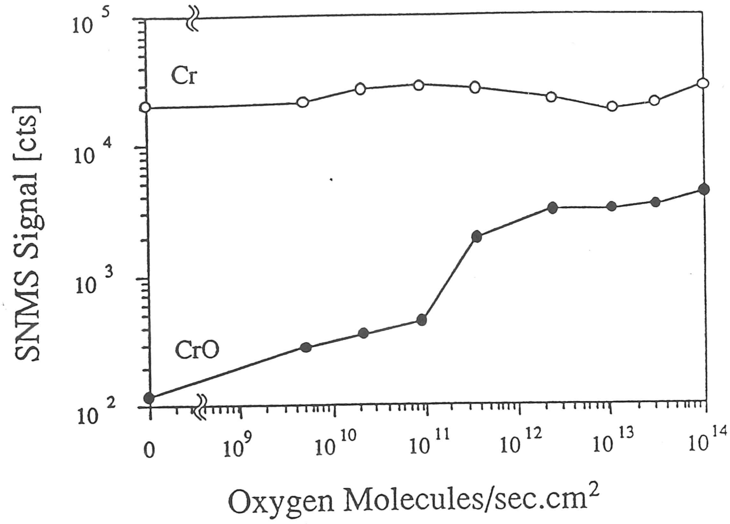

Figure 2: Relative SNMS yields of Cr and CrO under oxygen exposure of an initially clean polycristaline metal sample measured with pulsed 8keV Ar^+ beam of 1.6μA and pulsewidths of 20μsec(static conditions).

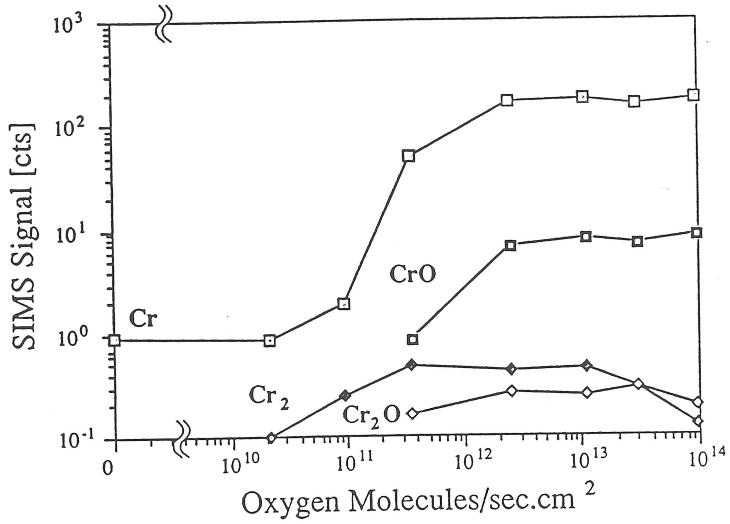

Figure 3: Relative SIMS yields of metal clusters Cr, Cr_2 and the oxides CrO and CrO_2 under oxygen exposure of an initially clean polycristaline metal sample measured with pulsed 8keV Ar^+ beam of 1.6μA and pulsewidths of 1μsec (static conditions).

atoms sputtered from a clean surface is $6.7 \cdot 10^{-4}$ for the dimer and $2.5 \cdot 10^{-4}$ for the trimer. The ratios remain constant until clusters disappear suddenly at a flux of 10^{11}oxygen molecules/sec·cm^2, coinciding with a rise of the oxide yield. The oxides start to rise at a flux of $2 \cdot 10^{10}$oxygen molecules/sec·cm^2 until the yields saturate at flux exceeding 10^{12}oxygen molecules/sec·cm^2. Although extensive sputter cleaning has been applied before each measurement, a considerable amount of oxygen (TaO and TaO_2) can be detected on a clean Ta surface. This may be caused by the residual pressure of CO in the chamber, the high affinity of Ta to absorb oxygen and the operation in static mode. The yield of Ta atoms decreases 25%, whereas the yield of the oxides TaO and TaO_2 increases by a factor of 12 and 11, respectively, for fully oxidized surface. Recently, a maximum of the yield of TaO was found at $2 \cdot 10^{-5}$mbar under dynamic conditions [10]. With higher doses the yield dropped again, because the probability to sputter a metal oxide decreases above a surface coverage of 0.5 [10]. In our experiment we observe also a small decrease of the TaO yield after the maximum at $2 \cdot 10^{12}$oxygen molecules/sec·cm^2, but of lesser size. A decrease of the Ta yield by a factor of 7 was found [10], which is considerably larger than what we observed in our experiment.

Discussion

The present results of the SNMS measurements for Cr differ considerably from previous results obtained by laser induced fluorescence [7]. With LIF, the yield of Cr ground-state atoms under simultanous oxygen exposure and Ar^+ bombardment was found to drop by a factor of hundred for a dynamic situation at $N_{gas}/N_{ion}=10$ [7,17]. The huge drop of ground-state atoms was explained by proposing that the sputtered flux from an oxidized surface consists mainly of oxide molecules. In general, in previous SNMS experiments a decrease approximately by a factor of 7 of the yield of metal atoms for oxidized surface was found. A possible explanation for the discrepancy can be a high rate of photo fragmentation of sputtered molecules in the ionizing region. The dissociation energy of the CrO molecule from the ground-state $^5\Pi$ is ≈4.0eV [18]. That is close to 4.02eV, the energy of a 308nm photon. Thus it seems most likely that one-photon dissociation of CrO occurs rather than ionization of the molecule. Fragmentation results with high probability in Cr^+ and O^- ions [18] due to the electronic configurationof the CrO molecule. Although ionization of Cr_2 $^1\Sigma_g$ only requires 1.86eV and is not close resonance, photo fragmentation can occur via an excitation to the $^7\Sigma_u{}^+$ antibonding potential curve [19]. This explains why in the special case of Cr and excitation with 308nm, only mi-

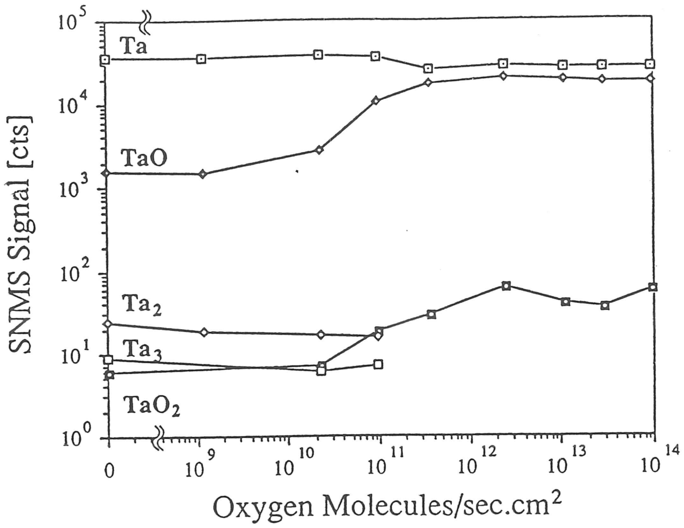

Figure 4: Relative SNMS yields of metal clusters Ta, Ta_2, Ta_3 and the oxides TaO and TaO_2 under oxygen exposure of an initially clean polycristaline metal sample measured with pulsed 8keV Ar^+ beam of 1.6μA and pulsewidths of 20μsec (static condi-

nor amounts of molecules are seen in the SNMS spectra.

Photo fragmentation seems to be a minor problem for Ta in our experiment. In a recent SNMS experiment a drop by a factor of 7 of the neutral Ta yield from an oxidized surface was found [10], but for dynamic conditions. As plasma ionization was employed there, differences in the obtained results can arise from the different ionization mechanisms, in particular concerning fragmentation of molecules. The reported ratio between Ta from a clean surface and TaO from a fully oxidized surface is only half the value we found. We used a higher primary ion energy, and it is known that the yield of TaO rises more than the Ta yield with energy [20].

Conclusions

Dissociation of molecules always poses a problem in ionization. For CrO and Cr_2 this seems to be much more pronounced than for Ta clusters as well as Ta oxides. Therefore, dissociation is a probable explanation why different results are obtained by different experimental techniques.

In conclusion the present result demonstrate that matrix effects for sputtered neutral metal atoms from oxides, even though they exist, are masked in SMNS to a high extend - depending on the ionization process and the particular metal-oxide system - due to fragmentation of sputtered molecules. As a consequence, the metal SMNS signal from oxides offers a better quantitative information about the particular metal concentration than matrix effects would imply.

Changing the wavelength of the ionizing laser, we have the possibility to optimize the ionization process to minimize photo fragmentation and thus obtain detailed information about the chemical structure of the surface and composition of the sputtered flux.

Acknowledgments

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References:

[1] A. Benninghoven, F.G. Rüdenauer, H.W. Werner, *Secondary Ion Mass Spectroscopy*, Wiley-Interscience Publication, Vol. **86** (1987)
[2] P. Williams, Appl. Surf. Sci., **13** (1982) 241
[3] R.E. Honig, J. Appl. Phys., **29** (1958) 549
[4] H. Oechsner, in: *Thin Solids and Depth Profile Analysis*, ed. H. Oechsner, Topics in Current Physics, Springer Verlag, Berlin, Vol **37** (1984) 63
[5] M.J. Pellin, C.E. Young, W.F. Calaway and D.M. Gruen,Surf. Sci., **144** (1984) 619
[6] C.H. Becker and K.T. Gillen, Anal. Chem. **56** (1984) 1671
[7] G. Betz, W. Husinsky, Nucl. Instr. Meth., **B13** (1986) 343
[8] E. Dullni, Appl. Phys., **A38** (1985) 131
[9] D. Grischkowsky, M.L. Yu, A.C. Balant, Surf. Sci., **127** (1983) 315
[10] A. Wucherer, H. Oechsner, Nucl. Instr. Meth., **B18** (1987) 458
[11] R. Kelly, Nucl. Instr. Meth., **B18** (1987) 388
[12] Peter Wurz, PhD. thesis, Technical University Vienna, (1990)

[13] P. Lambropoulos, Adv. At. Mol. Phys. **12** (1976) 87
[14] J. Morellec, D. Normand and G. Petite, Adv. At. Mol. Phys. **18** (1982) 97
[15] B.A. Mamyrin, V.I. Karataev, D.V. Shimkk and V.A. Zagulin, Sov. Phys. JETP, **37** (1973) 45, (English translation)
[16] A. Benninghoven, A. Mueller, Phys. Lett., **A40** (1972) 169
[17] W. Husinsky, G. Betz, Nucl. Instr. Meth., **B15** (1986) 165
[18] P.G. Jasien, W.J. Stevens, Chem. Phys. Lett., **147** (1988) 72
[19] M.M. Goddgame, W.A. Goddard, Phys. Rev. Lett., **54** (1985) 661
[20] H. Oechsner, H. Schoof, E. Stumpe, Surf. Sci. **76** (1978) 343