Note: Ion-induced secondary electron emission from oxidized metal surfaces measured in a particle beam reactor
Adrian Marcak, Carles Corbella, Teresa de los Arcos, and Achim von Keudell

Citation: Review of Scientific Instruments 86, 106102 (2015); doi: 10.1063/1.4932309
View online: http://dx.doi.org/10.1063/1.4932309
View Table of Contents: http://scitation.aip.org/content/aip/journal/rsi/86/10?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Contribution of surface plasmon decay to secondary electron emission from an Al surface

Calculated effects of work function changes on the dispersion of secondary electron emission data: Application for Al and Si and related elements
J. Appl. Phys. 110, 024906 (2011); 10.1063/1.3608046

Sharp reduction of the secondary electron emission yield from grooved surfaces

Work function of MgO single crystals from ion-induced secondary electron emission coefficient

Multiply charged ion-induced secondary electron emission from metals relevant for laser ion source beam diagnostics
Rev. Sci. Instrum. 73, 776 (2002); 10.1063/1.1431704
Note: Ion-induced secondary electron emission from oxidized metal surfaces measured in a particle beam reactor

Adrian Marcaj,1 Càrles Corbella,1,4 Teresa de los Arcos,2 and Achim von Keudell1
1Research Group Reactive Plasmas, Ruhr-University Bochum, 44801 Bochum, Germany
2Technical and Macromolecular Chemistry, Paderborn University, 33098 Paderborn, Germany

(Received 20 July 2015; accepted 22 September 2015; published online 1 October 2015)

The secondary electron emission of metals induced by slow ions is characterized in a beam chamber by means of two coaxial semi-cylindrical electrodes with different apertures. The voltages of the outer electrode (screening), inner electrode (collector), and sample holder (target) were set independently in order to measure the effective yield of potential and kinetic electron emissions during ion bombardment. Aluminum samples were exposed to quantified beams of argon ions up to 2000 eV and to oxygen atoms and molecules in order to mimic the plasma-surface interactions on metallic targets during reactive sputtering. The variation of electron emission yield was correlated to the ion energy and to the oxidation state of Al surfaces. This system provides reliable measurements of the electron yields in real time and is of great utility to explore the fundamental surface processes during target poisoning occurring in reactive magnetron sputtering applications. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4932309]

Secondary electron emission (SEE) plays a central role in the generation and sustaining of glow discharges.1,2 The collision of primary particles such as electrons, ions, photons, and metastables against a surface constitutes the source of secondary electrons. Moreover, the SEE coefficient, γ, which is defined as the ratio between secondary electrons current and incident ion current, strongly depends on the chemical state of the target surface, which is modified by the impinging reactive species. In the past, several experimental setups were used to study γ of different materials in real time. For instance, I-V measurements in conventional sputtering reactors yielded γ estimations after some modeling.3 Also, I-V characteristics from technological plasmas were measured with a retarding field analyzer operated with determined grid potentials. As a result, the individual contributions of the primary particle beams to the SEE production were obtained separately.4 However, the oxidation state of the sample could not be regulated in this setup.

The objective of the present work consists in characterizing the SEE during reactive sputtering of Al targets. For this, vacuum beam experiments have been performed in order to mimic basic processes of a surface in contact with plasma. The beam chamber has been adapted using a special arrangement of electrodes, which permits the evaluation of SEE coefficient through simultaneous measurements of ion current on the sample and secondary electron current on a collector.

The generation of secondary electrons has been studied in an ultra-high-vacuum particle beam reactor thoroughly described elsewhere, which is equipped with an electron cyclotron resonance (ECR) plasma source and an oxygen beam source (OBS).5 Base pressure was lower than 5 · 10−6 Pa. The sample holder has been conveniently modified. The SEE-module consists of three electrodes made of stainless steel which can be independently biased: screening, collector, and holder, which are assembled as depicted in Fig. 1. The approximate radius of the set is 30 mm, and it has 110 mm in height. The two semi-cylindrical coaxial electrodes, with apertures for the particle beams, are separated by a 2 mm gap and surround the sample surface, which constitutes the third electrode. Screening and sample holder are grounded, whereas the collector is biased to positive voltages. The sample consisted of a 25 μm-thick Al foil cut out with 99.999% purity. These are the main features and purposes of the electrodes.

• Screening (outer electrode): It is maintained at ground potential (0 V) as shielding of the collector electrode from the incoming ion beam. The extension of the screening electrode was optimized by simulating ion trajectories from the ECR plasma source to sample with SIMION 8.1 software. The cylindrical hull on the ion aperture and the relatively large surface area of the screening electrode avoided ion beam collision onto the collector.

• Collector (inner electrode): It captures the secondary electrons emitted on the sample due to ion impact. The SEE total current over the whole area, Icollector, is measured with a multimeter. Thus, the measurements constitute an integration of the SEE angular distribution. The ion aperture is located in the direction where SEE is maximized (normal to sample), which provokes an underestimation of this current. The positive bias (ca. +10 V) is applied to attract effectively the electrons emitted from the sample.

• Holder: The Al foil is fastened on the sample holder with clamps. This electrode is grounded and possesses a lateral track that permits to insert and extract samples using the load-lock chamber. The total current, Isample, is measured with a second multimeter. Typical values of ion flux are between 1013 and 1015 cm−2 s−1 corresponding to an irradiated surface area of ≈1 cm2.

Author to whom correspondence should be addressed. Electronic mail: carles.corbella@rub.de.

1Department of Physics, University of New Mexico, 87131 Albuquerque, New Mexico, USA. 2Department of Chemical Engineering, University of New Mexico, 87131 Albuquerque, New Mexico, USA. 3Department of Chemical Engineering, University of New Mexico, 87131 Albuquerque, New Mexico, USA. 4Department of Chemical Engineering, University of New Mexico, 87131 Albuquerque, New Mexico, USA.
According to this electrode configuration, the SEE-coefficient is defined as follows:

$$\gamma = \frac{I_{\text{collector}}}{I_{\text{sample}} - I_{\text{collector}}},$$

where we have assumed that $I_{\text{ion}} = I_{\text{sample}} - I_{\text{collector}}$, i.e., secondary electrons are not lost between their emission from the sample surface and capture on the collector.

Fig. 2 shows the influence of the set ion energy on the collector current, the sample current, and the SEE coefficient, $\gamma$. The sample was always pre-sputtered with energetic argon ions for at least 15 min to eliminate the contamination layer. Measure of weakly oxidized Al surfaces provided higher SEE coefficients, since $\text{Al}_2\text{O}_3$ possesses higher secondary electron emissivity than metallic Al (see the work of Depla et al.).

The endpoint of Al pre-sputtering was the achievement of minimal SEE.

The total current $I_{\text{sample}}$ measured at very low ion energies sets the reference value due to photoelectron emission, since the primary beam in these conditions is basically formed by UV photons originated in the ECR plasma. Therefore, any measurement of sample current shows an offset that corresponds to the sample current due only to photons. Such offset must be subtracted from the total current on the sample. In view of the very low sample currents at weak ion bombardment conditions ($E_i < 200$ eV), the contribution of UV radiation can be neglected in front of ion current, similarly to a previous study. Although the Ar metastable emission is around 12 eV, this result reveals a very low or negligible flux of UV photons with energies higher than the work function of Al (4.28 eV).

Large oscillations of $\gamma$ were obtained at $E_i < 250$ eV due to the creation of secondary electrons by the ECR plasma source itself when low-energy ions hit the ion optics grids. Such electrons interfere with the measured flux of secondary electrons generated at the target. Therefore, this region has not been studied. Collector current (Fig. 2(a)) increases monotonically with ion energy, whereas sample current (Fig. 2(b)) increases up to a maximum of 100 $\mu$A at around 1000 eV. At higher energies, sample current saturates. This behavior probably owes to underestimation of total impinging Ar flux (ions and neutrals) due to recombination of Ar$^+$ species just before reaching target surface. This effect is possibly caused by (1) charge-exchange collisions between Ar ion beam and sputtered Al atoms and (2) recombination of Ar ions with the emitted secondary electrons. Measurements of the neutral particle flux would help to clarify this issue. Also, the change from potential electron emission (PEE) to kinetic electron emission (KEE) at around 1000 eV modulates the evolution of $\gamma$ with ion energy.

In fact, opposed to the more isotropic PEE, KEE mechanisms are similar to ion sputtering, which might provide secondary electron beams well aligned to the orthogonal direction of the sample surface. Unfortunately, this direction is not covered by the collector due to the ion aperture and it may be the reason why a lower SEE current than expected is measured.

The values of the SEE-coefficient (Fig. 2(c)), $\gamma$, which have error bars limited to $\approx 25\%$, are consistent with the order of magnitude reported in the literature, i.e., $\approx 0.1$. As suggested above, the relatively low values of $\gamma$ may be caused by the presence of the electrode aperture for ions. Indeed, the angular distribution of the secondary electron current is maximal at the direction of the aperture (normal with respect to sample), which yields a systematic underestimation of $\gamma$. Interestingly, a minimum of this parameter is located at around 1000 eV. The increase of $\gamma$ at higher ion energies points to an increase of SEE efficiency probably due to the above-mentioned underestimation of arriving Ar atoms and ions. On
the other hand, the increase of \( \gamma \) observed at lower ion energies may be associated to the measured low \( I_{\text{col}} \) values. Such increase could be also related to the instantaneous formation of an oxide layer during ion bombardment. However, the formation time of an oxide (contamination) monolayer at \( 5 \times 10^{-6} \text{ Pa} \) of background pressure is roughly estimated to be 50 min, considering an oxygen sticking coefficient on Al of 0.015.\(^{10,11}\) Therefore, surface contamination is discarded as mechanism enhancing \( \gamma \).

The behavior of \( \gamma \) on partially oxidized surfaces is governed by the oxidation degree. In the case of oxides that sputter congruently (no sub-oxides are formed), \( \gamma \) is parameterized with the oxide fraction at the surface, \( \Theta \), which is defined in the context of the Berg’s model.\(^9,12\)

\[
\gamma = \Theta \times \gamma_{\text{oxide}} + (1 - \Theta) \times \gamma_{\text{metal}}. \tag{2}
\]

In this work, oxidation of Al surface was achieved by sending beams of oxygen atoms and molecules to the sample during ion bombardment (mass flow rates from 0.10 to 0.50 SCCM). Although charging up of sample surface to a certain extent is possible due to surface oxidation, significant screening of the incident ions is not expected since the oxide top layer formed during sputtering is very thin (\( \approx 5 \text{ nm} \)).\(^{10}\) Fig. 3 depicts SEE coefficients as function of oxygen flux onto sample surface, \( j_{O_2} \). Saturation of \( \gamma \) took place already at low oxygen fluxes, indicating fully oxidation of the Al surface. Such saturation is correlated to the high oxygen implantation calculated by Kreiter et al. from quartz microbalance measurements in combination with Fourier transform infrared (FTIR) spectroscopy in the same beam reactor.\(^{11}\)

A strong increase of SEE coefficient is observed at all ion energies due to ion implantation: knock-on effect is evident given the steep increase at \( j_{O_2} \approx 10^{16} \text{ cm}^{-2} \text{s}^{-1} \). Besides the measured \( \gamma \) values for \( \text{Al}_2\text{O}_3 \) are similar to those provided in the literature (\( \approx 0.19 \)), there is a factor 2 between metallic and oxidized states, showing that the measurements are reliable. Small deviations from the literature values are caused mainly by surface roughness variations during process and the electrode configuration itself. Indeed, there is a complex dependence of SEE on surface roughness of the sample.\(^{13}\) This effect may explain the observed mismatches of \( \gamma \) values at oxygen flow zero between Figs. 2 and 3. On the other hand, a systematic underestimation of \( \gamma \) owes to the location of the ion aperture, which avoids the collection of the main stream of secondary electrons.

In summary, particle beam experiments permitted to characterize SEE of an Al surface exposed to quantified beams of argon ions and oxygen atoms and molecules. The behavior of SEE is discussed as function of the ion beam energy and has been correlated to the oxidation state of Al. This work describes a relatively simple instrument that provides straightforward and reliable measurements of \( \gamma \) of metallic targets as function of their oxidation degrees.

The authors thank the technical support of N. Grabkowski. Also, the financial support of the German Research Foundation through the coordinated centre No. SFB-TR 87 is acknowledged.


