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Ion-induced oxidation of aluminum during reactive magnetron sputtering

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Particle beam experiments were conducted in an ultra-high-vacuum vessel to mimic target poisoning during reactive magnetron sputtering of aluminum. Aluminum targets were exposed to quantified beams of argon ions, oxygen atoms and molecules, and aluminum vapour. The growth and etch rates were measured in situ by means of an Al-coated quartz crystal microbalance. The chemical state of the target surface was monitored in situ by real-time Fourier transform infrared spectroscopy. The surface processes were modelled through a set of balance equations providing sputter yields and sticking coefficients. The results indicate that the oxygen uptake of the aluminum surface is enhanced by a factor 1 to 2 by knock-on implantation and that the deposition of aluminum is not affected by the oxidation state of the surface. © 2013 American Institute of Physics.

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I. INTRODUCTION

Plasma deposition processes using reactive magnetron sputtering (RMS) are of major importance for many present day technologies. A prominent example is the deposition of aluminum oxide, which is used as heat insulation on glass or as hard coatings on tools. In RMS, an aluminum target is sputtered by an intense argon plasma and the sputtered atoms condense on the substrate to be coated. By adding oxygen to the discharge, oxygen molecules as well as oxygen atoms react at the substrate surface and the compound aluminum oxide is formed. By adjusting the ion bombardment on the substrate, the film morphology and properties can be tuned.

The addition of oxygen also causes hysteresis effects in RMS processes due to oxidation of the target surface. This hysteresis of the operating parameters of RMS is now well understood and is modelled by a set of balance equations for the oxygen surface coverage, as pioneered by Berg and Nyberg. The fundamental surface processes in these models are (1) chemisorption of oxygen atoms and molecules on the target and on the substrate, (2) sputtering of the metal and the oxide, and (3) knock-on implantation of oxygen by the ion bombardment. The input parameters for this model have been measured recently by Kuschel and von Keudell using quantified particle beam experiments employing beams of argon ions, oxygen atoms and molecules. The sticking coefficients for oxygen, the sputtering yields for aluminum and for aluminum oxide were consistent with the literature. However, an ion-enhanced chemisorption of oxygen molecules to the growing film surface was found. This could be modelled by the process of knock-on implantation, where an incident ion transfers surface bonded oxygen into subsurface regions, whereby new adsorption sites at the surface are being created.

In this paper, we address the ion-enhanced oxidation of an aluminum target more thoroughly, by upgrading our previous experiment regarding two aspects: (i) adding an aluminum atom source to mimic also aluminum re-deposition at the target surface during magnetron sputtering, and (ii) investigating the surface with in situ real time infrared spectroscopy, to directly monitor the upbuild of oxygen on the surface.

The good agreement between data and modeling in Ref. 7 was achieved by postulating an efficiency for knock-on implantation of the order of unity, although TRIDYN simulations, as presented in Ref. 7, indicated an efficiency of only $\geq 0.1$ at an ion energy of 400 eV. The experimental determination of the efficiency for knock-on implantation in Ref. 7 is debatable, because surface processes at almost metallic aluminum targets are analyzed with the oxidation being only a small perturbation. Any ion-enhanced oxidation processes, however, should be most relevant for highly oxidized aluminum targets. To resolve this issue, we operate in this paper the beam experiment with fluxes leading to a strongly oxidized surface while also in situ monitoring the oxidation state.

Any oxidation process depends also on any additional flux of aluminum atoms onto the target, which act as a sink for incident oxygen species. This additional flux of aluminum might be caused in our beam experiment by the ongoing sputtering of the aluminum surfaces followed by a re-deposition of the sputtered material. As a consequence, an apparent ion-enhanced oxygen uptake would be deduced, if the aluminum re-deposition is not taken into account. Such aluminum re-deposition should be minimal, because the mean-free-paths are of the order of the chamber dimensions in the beam setup. The surface oxidation of deposited aluminum, however, can more directly be excluded by intentionally adding an aluminum atom source to the experiment. If we assume a sticking coefficient of unity for incident aluminum atoms, any enhanced oxidation due to additional aluminum at the surface should scale with the incident aluminum atom flux to the surface. If any ion-induced re-deposition plays a role, a deviation from this simple scaling should be observable.

Finally, these proposed experiments test also the validity of the model from Ref. 7 by extending it to an oxidic regime of the target. It is interesting to see whether all input parameters such as sputtering yields for aluminum and oxide as well as sticking coefficients for oxygen and aluminum can be kept identical and only the major unknown parameter, namely, the efficiency for knock-on implantation can be assessed more directly.
II. EXPERIMENTAL DETAILS

Fig. 1 shows a top view of the ultra-high-vacuum (UHV) chamber housing the substrate holder and the particle sources being pumped by a turbomolecular pump (TMP) and an ion getter pump (IGP). The base pressure was approximately $10^{-5}$ Pa. Prior to each experiment, the vacuum system was baked out at temperatures between 120 °C and 150 °C for 8 h. Three particle sources are installed, namely, a plasma ion source, a thermal oxygen atom source, and an aluminum effusion cell. Growth and etch rates were measured using a quartz crystal microbalance (QCM) with a shutter in front of the QCM to stop the particle beams and define thereby the start and the end of an experiment. The working pressure when the gases were admitted to the setup was always of the order of a few $10^{-2}$ Pa resulting in a mean free path of particles larger than the distances between sources and target.

The QCM consisted of AT-cut quartz crystal resonators (0.5 mm thickness and 14 mm diameter) with an Al coating of 1 μm thickness. Any temperature induced drifts of the QCM measurements were suppressed by proper water-cooling during the whole experiment. Two QCMs were installed in the holder (dual unit), and their resonance frequencies were recorded simultaneously. A built-in two position shutter selected one crystal being exposed to the particle beams.

The Ar⁺ ion beam is produced by an electron cyclotron resonance (ECR) plasma source. The ions from this plasma were extracted using a double grid system. The ion flux was measured with a Faraday cup yielding fluxes between $10^{13}$ cm⁻² s⁻¹ and $10^{14}$ cm⁻² s⁻¹. The diameter (FWHM) of the ion beam is about 20 mm, as being determined from the etch profile of a hydrocarbon film deposited onto 26 mm² c-Si after being bombarded by Ar⁺ ions at 400 eV.

It is worth noting that the absolute particle fluxes in beam experiments are usually orders of magnitude lower compared to the plasma counterparts. However, the important parameter to assess target poisoning processes is the ion-to-neutral flux ratio. In addition, the rate equations that model these processes are linear in the incident particle fluxes. These parameters permit to simulate plasma conditions, although the particle beam experiment employs only low particle fluxes.

The oxygen beam source (OBS) is based on dissociation of oxygen molecules in an iridium capillary heated to 1800 °C producing a focused beam composed of atomic and molecular oxygen. At this temperature, the total flux of oxygen from the source is composed of 15% atoms and 85% of oxygen molecules from the gas background yielding a flux of oxygen atoms in the order of $10^{14}$ cm⁻² s⁻¹. In addition, the oxygen background pressure could be kept about a few $10^{-3}$ Pa, yielding a background flux of oxygen molecules in the order of $10^{15}$ cm⁻² s⁻¹.

Al atoms are provided by an effusion cell equipped with a cooling shroud and a shutter. Although the melting temperature of the Al pellets is 670 °C, the vapor pressure starts to increase exponentially only between 900 °C and 1200 °C. The selected working temperatures were 1060 °C, 1100 °C, and 1130 °C, yielding fluxes of $3.0 \times 10^{13}$ cm⁻² s⁻¹, $6.3 \times 10^{13}$ cm⁻² s⁻¹, and $1.1 \times 10^{14}$ cm⁻² s⁻¹.

The incident oxygen flux is 1-2 orders of magnitude higher than the aluminum flux. Based on typical sticking coefficients of 0.015 for oxygen and 1 for aluminum, an almost identical incorporation rate of aluminum and oxygen is obtained being optimal for studying aluminum targets in their oxidized state.

The exposure of Al films to the particle beams was also measured in real time using in situ Fourier transform infrared spectroscopy (FTIR) in reflection mode at an angle of incidence of 70°, to monitor the longitudinal and transversal-optical excitations of Al₂O₃-bonds in the film surface. The IR beam is guided through the setup via KBr windows and is recorded by an external liquid N₂-cooled MCT detector. The samples consisted of Al films (1 μm) deposited at room temperature onto e-Si wafers by magnetron sputtering. At first, a FTIR background spectrum $R_0$ is measured. Then, the FTIR spectra $R$ are continuously sampled during exposure of the Al film to the particle beams with a time resolution of 30 s. Each sample spectrum $R$ is referenced to the initial background spectrum $R_0$. The etching and oxidation state of the film become visible as a variation in reflectivity at a wavenumber around 950 cm⁻¹ characteristic for Al₂O₃ vibrations.

The change in IR absorption is monitored during the simultaneous treatment with argon ions and oxygen atoms and molecules until the surface reaches a steady oxidation state. The resulting steady state peaks are measured at different oxygen fluxes and are then compared with the peak of the “natural” oxide being formed by adding only 0.5 sccm of oxygen through the capillary of the oxygen source without any ion bombardment. Prior to this exposure, the Al surface was cleaned by 5 min argon sputtering at 800 eV.

The beam experiments were performed in two configurations: (1) QCM configuration: the QCM facing the OBS resulting in an angle of incidence of the ion beam of 45° to the surface normal and of the Al beam of 60° to the surface normal, respectively. Prior to each experiment, the substrates were bombarded by Ar⁺ at 800 eV for 10 min to remove any pre-existing passivation layer of Al₂O₃. This procedure was validated by monitoring the QCM until a steady state etching rate is reached indicating the sputtering of a fresh Al surface with sputter yields being identical to literature values for Ar⁺ bombardment of clean Al, and (2) FTIR configuration:
the substrate holder facing the ion beam with the oxygen beam at 45° to the surface normal, the Al source was not used in this case. The aluminum surfaces were refreshed by sputtering the oxide completely, which was monitored by simultaneous FTIR measurements. Additionally, each measurement was performed on a new aluminum sample to ensure identical initial conditions. The quantified ion and atom/molecule fluxes are corrected by a cosine law for the different angles of incidence.

III. RESULTS AND DISCUSSION

A. Modeling

The surface processes during the combined impact of ions, oxygen molecules, and aluminum atoms are modelled with a set of balance equations. The surface of the target is separated into a metallic and an oxidic part, expressed by a coverage Θ. The following elementary processes are implemented:

- **Sputtering**: Sputtering of aluminum or aluminum oxide by argon ions is modelled by sputter yields $Y_{Al}$ and $Y_{O}$, respectively. The sputter yields $Y_{Al}$ at 45° of beam incidence (config. QCM) were 1.55 and 2.42 for 400 eV and 800 eV, respectively. The sputter yields $Y_{Al}$ at 0° of beam incidence (config. FTIR) were 0.59 and 0.95 for 400 eV and 800 eV, respectively. The sputter yields were determined by SRIM simulations and are in good agreement with the literature. \(^1\) We approximated $Y_{O} \approx 0.1 \cdot Y_{Al}$ consistent with the literature. \(^12,13\)

The parameter $Y_{O}$ describes a process consisting of an ion-induced removal of an AlO$_2$ surface group and/or the preferential sputtering of oxygen only. In both cases, an oxidized surface site is converted into a metallic surface site.

- **Chemisorption of oxygen**: Dissociative chemisorption of oxygen molecules on aluminum covered surface sites is modelled by a sticking coefficient $s_{O_2}$, being $s_{O_2} = 0.014$. \(^7,14–16\) We only considered the sticking of O$_2$ molecules since the background pressure dominated over the directed flux of O atoms.

- **Chemisorption of aluminum**: Chemisorption of aluminum on oxidic and on metallic surface sites is modelled by sticking coefficients $s_{Al} \approx 1$. This value is in good agreement with the findings in the literature. \(^17\)

- **Ion-enhanced chemisorption**: The ion bombardment during exposure of aluminum to the beams may enhance the efficiency of oxygen chemisorption by the effect of knock-on implantation. Ions may transfer already deposited and bonded oxygen on the surface into subsurface regions within a collision cascade. Hence, sites on the surface are depleted and become available to chemisorb the newly arriving oxygen species. This effect is quantified by a variable $k$. This parameter has been determined from mass variation rates as measured with the QCM and from the state of oxidation as studied by FTIR.

\[ n_0 \frac{d \Theta}{dt} = -Y_{O} j_{Ar^+} + 2s_{O_2} (1 - \Theta)^2 j_{O_2} - k j_{Ar^+} - s_{Al} j_{Al} \]  

(1)

In steady state, the coverage of $n_0$ as areal density of surface sites can be calculated yielding a mass variation rate $\Gamma_{\text{total}}$ as measured by the QCM of

\[ \Gamma_{\text{total}} = -Y_{Al} (1 - \Theta) j_{Ar^+} - Y_{O} j_{Ar^+} + 2s_{O_2} (1 - \Theta)^2 j_{O_2} + s_{Al} j_{Al} \]  

(2)

B. Growth and etch rates

Absolute growth and etch rates were measured by QCM in configuration QCM. Fig. 2 shows the growth rates, expressed in deposition fluxes in cm$^{-2}$s$^{-1}$, for exposing aluminum to the combined impact of argon ions at 400 eV

\[
\begin{align*}
E_{ions} &= 400\text{ eV} \\
\dot{j}_{Ar^+} &= 6.7 \times 10^{-13} \text{ cm}^{-2} \text{s}^{-1} \\
\dot{j}_{Al} &= 3.0 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1} \\
\dot{j}_{Al} &= 6.3 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1} \\
\dot{j}_{Al} &= 1.1 \times 10^{14} \text{ cm}^{-2} \text{s}^{-1}
\end{align*}
\]

(a)

\[
\begin{align*}
E_{ions} &= 800\text{ eV} \\
\dot{j}_{Ar^+} &= 9.9 \times 10^{-13} \text{ cm}^{-2} \text{s}^{-1} \\
\dot{j}_{Al} &= 3.0 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1} \\
\dot{j}_{Al} &= 6.3 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1} \\
\dot{j}_{Al} &= 1.1 \times 10^{14} \text{ cm}^{-2} \text{s}^{-1}
\end{align*}
\]

(b)

FIG. 2. Effective deposition fluxes during reactive sputtering of Al by Ar$^+$ and O$_2$, together with deposition of Al vapour at (a) 400 eV and (b) 800 eV. The lines denote the results of the rate equation model using the following parameters: $s_{O_2} = 0.014$, $s_{Al} = 1$, $k = 0.96$ (a) and 1.48 (b), $Y_{Al} = 1.55$ (a) and 2.42 (b), $Y_{O} = 0.1 \cdot Y_{Al}$.
(Fig. 2(a)) and 800 eV (Fig. 2(b)), of aluminum atoms and of oxygen molecules at varying fluxes. The frequency shift of the QCM is converted into mass variation by means of the Sauerbrey equation. The deposition fluxes are obtained from the mass variation rate by considering the atomic mass and the density of the aluminum film on the quartz crystals.

Fig. 2 shows also the modelled rates based on Eq. (2) using the fitting parameters as being listed above. One can see that the order of magnitude of the rates is perfectly reproduced by the model. However, the dependence on the oxygen flow is much stronger at low fluxes in the model compared to the data.

The model reproduces the data only with limited accuracy. A better fit could be achieved by choosing very much higher sticking coefficients of the order of 0.05 instead of 0.015. Such high sticking coefficients are in contradiction to the modeling in Ref. 7, where the pure oxidation of a freshly sputtered aluminum surface has directly been analyzed. Here, however, sputtering of a strongly oxidized target is modeled, where the separation of the surface into a metallic part and an oxidic part might be too simple to yield an excellent fit. Any more detailed surface site modeling of a strongly oxidized target is beyond the scope of this paper. Nevertheless, in contrast to the cold ground state particles used here, higher sticking coefficients are expected in the case of hyperthermal particles, which are likely to be present in plasma processes. Indeed, the sticking coefficient increases rapidly with the energy of molecules.

The experimental results show significant deposition of aluminum oxide even at small oxygen fluxes, while the model predicts very small deposition rates or even etching (at 800 eV). For higher oxygen fluxes, the dependence of the oxygen flux on the deposition flux is over-estimated by the model, as the experimental data show only small changes in the deposition rate. The differences in the deposition rates resulting from the different aluminum fluxes are reproduced by the model very well. This illustrates that aluminum deposition on the target can be described very simply by a sticking coefficient, which does not depend on the oxygen coverage.

A sticking coefficient of unity for aluminum atoms is consistent with expectations from the literature, although it has never been directly measured under ion bombardment conditions. In addition, distinct sticking coefficients for aluminum sticking on metallic vs. oxidized surface sites are apparently not necessary. Finally, the oxygen uptake of a surface being simultaneously exposed to incident aluminum atoms is apparently quantitatively described by the rate equation model. Consequently, any ion-induced aluminum re-deposition processes do not contribute to our beam experiment.

C. Ion-enhanced oxidation studied by FTIR

A further insight in the surface processes can be reached by analyzing the surface being exposed to the beams of argon ions and oxygen atoms/molecules using infrared spectroscopy, as shown in Fig. 3. A reference spectrum from an experiment exposing aluminum to oxygen only is added (solid line in Fig. 3). In all experiments, the exposure causes an initial fast increase in absorption due to the generation of the oxidized surface. This is followed by a smaller steady state oxidation rate, as shown in Fig. 2. The infrared spectra in Fig. 3 are corresponding to the formation of the oxidized surface in steady state.

Since the information depth of infrared spectroscopy is of the order of the wavelength, AlO$_x$ groups at the very surface as well as in the subsurface region are monitored. This total amount of oxygen incorporated in the surface in steady state can be expressed as

$$n_{\text{AlO}_x} = \Theta \cdot n_0 + k\Theta \cdot n_0.$$  

The first term describes the oxygen at the surface, and the second term accounts for the oxygen located in the subsurface region, as being, for example, subplanted by knock-on implantation. The density of oxygen groups $n_{\text{AlO}_x}$ being formed during oxidation is directly correlated to the change on infrared reflectivity $R/R_0$ integrated over the wavenumber region of IR absorption: $n_{\text{AlO}_x} \sim \int (1 - R/R_0) = I_{\text{ion-induced}}$. If we assume that a surface density $n_0$ of oxygen groups is created by exposing aluminum to oxygen only, yielding $I_{\text{thermal}}$, we can deduce the number of oxygen groups being created by an additional ion bombardment via

$$\frac{I_{\text{ion-induced}}}{I_{\text{thermal}}} = \frac{n_{\text{AlO}_x}}{n_0}.$$  

FIG. 3. FTIR spectra $R/R_0$ during reactive sputtering of Al at (a) 400 eV and (b) 800 eV, at different oxygen flows. The solid line denotes the spectra if the oxygen source is used only at its maximum flow rate of 0.5 sccm.
By measuring the spectra $R/R_0$ for different degrees of oxidation, we can compare a predicted value for $n_{\text{AlO}}/n_0$ using Eq. (3) with a coverage $\Theta$ as being given by Eq. (1) with the measured values for $n_{\text{AlO}}/n_0$ from Eq. (4). The same parameters as in the QCM measurements were used (see Fig. 2), only the parameter $k$ for 400 eV and 800 eV was determined by fitting the measured data. The comparison is shown in Fig. 4, where one can see an excellent agreement.

The parameter $k$ for ion-induced enhancement of oxygen chemisorption varies between 1 at 400 eV and 1.5 at 800 eV. These values are smaller than the values presented in Ref. 7 ($k = 3$ at 400 eV and $k = 4$ at 800 eV), where QCM data were modeled for the metallic regime. This discrepancy may be caused by the fact that in Ref. 7 the metallic regime has been modeled. Here, however, the data are measured in the oxidic regime with a dominant oxide growth and presumably a rather small metallic surface fraction. We can conclude that the efficiency $k$ takes different values depending on the explored regime. The lower values of $k$ in RMS at the oxidic regime point to a less efficient knock-on implantation compared to the metallic regime. This result might be related to the dependence of the implantation efficiency on the stoichiometry of the material. Since the oxide density is relatively high, a collision cascade could also transport oxygen from bulk back to the surface, resulting in a lower efficiency in knock-on implantation, and, therefore, in a smaller estimated value of $k$.

The ion bombardment may induce changes in surface morphology such as the creation of a surface roughness or voids. This leads to an increase in reactive area of the surface, making it more accessible to incident oxygen. This effect would also contribute to an apparent high knock-on parameter $k$. AFM measurements were performed to investigate this effect, yielding RMS-values of only 9.03 nm on an untreated aluminum sample; 8.62 nm on a sample treated at simultaneous impact of argon ions at 400 eV and oxygen atoms/molecules; and 7.74 nm on a sample treated at simultaneous impact of argon ions at 800 eV and oxygen atoms/molecules. Consequently, the surface remains very flat for our experimental conditions irrespective of the ion bombardment.

IV. CONCLUSIONS

QCM experiments at room temperature in a particle beam reactor have been applied to mimic target poisoning in reactive sputtering of aluminum oxide. The total sputtering rate of an Al target by Ar$^+$ was quantified and modified by simultaneously evaporating Al from an effusion cell. Measurements of mass variation rate during simultaneous bombardment with oxygen atoms and molecules showed an enhanced oxidation described by a surface coverage model. The ion-enhanced oxidation was additionally studied by in-situ FTIR. These results were successfully fitted with the same parameters that were used for modeling of the mass variation rates measured by QCM. All input parameters for the model can directly be measured in the beam experiment yielding values, which are consistent with literature values.

The beam experiments verified thereby the validity of the rate equation model from Ref. 7 by extending it to an oxidic regime of the target. All input parameters such as sputtering yields for aluminum and oxide as well as sticking coefficients for oxygen and aluminum are consistent with the literature values. The efficiency for knock-on implantation is directly measured to unity, which is well above the prediction by TRIDYN of the order of only $\approx 0.1$. This discrepancy cannot be resolved and requires more direct surface science experiments on oxidized aluminum surfaces. Nevertheless, the presented set of input parameters is very robust and can be regarded as universal for modeling the hysteresis in industrial reactive magnetron processes.

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4Sputter Yield Values listed by National Physical Laboratory, 2012.