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Formation of crystalline $\gamma$-$\text{Al}_2\text{O}_3$ induced by variable substrate biasing during reactive magnetron sputtering

M Prenzel$^1$, A Kortmann$^1$, A von Keudell$^1$, F Nahif$^2$, J M Schneider$^2$, M Shihab$^3$, R P Brinkmann$^3$

$^1$ Research Group Reactive Plasmas, Ruhr-Universität Bochum, D-44780 Bochum, Germany
$^2$ Materials Chemistry, RWTH Aachen University, D-52056 Aachen, Germany
$^3$ Theoretical Electrical Engineering, Ruhr-Universität Bochum, D-44780 Bochum, Germany

E-mail: marina.prenzel@rub.de

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Abstract

Reactive magnetron sputtering is a widely used technique to deposit various materials such as oxides and nitrides with a superior control of morphology and stoichiometry. The adjustment of the film properties at a given substrate temperature is believed to be affected by the average energy $\langle E \rangle$ per incorporated atom during film growth, which is controlled by the ion-to-neutral ratio in the film forming growth flux and the energy of the incident ions. This concept is tested for alumina growth in an rf-magnetron discharge by keeping $\langle E \rangle$, the average energy of the incident ions $E_{\text{ions}}$, and the ion-to-neutral flux ratio constant, but varying only the energy distribution of the incident ions (ion energy distribution–IED). The influence of the IED on film growth is monitored by observing the transition of the films between x-ray amorphous $\text{Al}_2\text{O}_3$ to $\gamma$-$\text{Al}_2\text{O}_3$. The results reveal that the substrate temperature necessary for the transition to $\gamma$-crystalline films can be lowered by almost 100 °C, when the maximum energy of the incident ions is kept at 100 eV, while maintaining the energy per incorporated atom at 11 eV. This result is compared with TRIM calculations for the collision cascades of impacting ions.

(Some figures may appear in colour only in the online journal)

1. Introduction

Reactive magnetron sputtering (RMS) is a widely used technique to deposit many thin film materials, such as for example oxides and nitrides using metal targets and the addition of oxygen and/or nitrogen as a reactive component to the argon plasma gas. The film stoichiometry and its structure can be adjusted by controlling the ion-to-neutral ratio in the film forming growth flux and the energy of the incident ions given by the ion energy distribution (IED) function.

This interplay between ion bombardment and material properties has been intensely investigated in the past, resulting in the common belief that an ion-induced enhancement of the adatom mobility promotes crystallinity and/or a certain crystalline orientation. This ion-induced enhancement is often quantified using a single parameter, namely the energy per deposited atom $\langle E \rangle$. This energy depends on the ion energy $E_{\text{ions}}$ and on the ion-to-neutral ratio $J_{\text{ions}}/J_{\text{growth}}$ in the growth flux with $\langle E \rangle = E_{\text{ions}} \cdot J_{\text{ions}}/J_{\text{growth}}$. $J_{\text{ions}}$ is the flux of incident ions and $J_{\text{growth}}$ the total flux of incorporated atoms in the film.

Petrov et al [1, 2] concluded that the average energy per atom is clearly not a universal growth parameter. In more detail, the dependence of the crystal orientation of titanium nitride (TiN) on $\langle E \rangle$ was analysed. They varied the ion energy and kept the ion-to-neutral ratio constant. In a second experiment, the ion energy was kept constant and only $J_{\text{ions}}/J_{\text{growth}}$ was changed. In both cases, $\langle E \rangle$ is varied. A small ion-to-neutral ratio and an ion energy of 85 eV resulted in a preferred orientation of the deposited TiN films. Petrov et al concluded that it is essential that ions are stopped within the first monolayers to efficiently promote adatom mobility. This sets boundaries not only on the ion-to neutral ratio but also on the absolute energy of the ions.
The exact details of these ion-induced surface processes, however, remain still unclear. Although, one can devise an experiment providing a unique energy per deposited atom (E), and a constant ion-to-neutral ratio, film growth may still depend on more subtle effects such as the particular IED and/or the temporal sequence of the incident species. In the case of pulsed plasmas and/or pulsed bias concepts, the sequence of adsorption of neutral species and of the ion-induced densification of the film may occur simultaneously or sequentially which may affect structure evolution. The most prominent example in that respect is HPPMS plasmas [3], where a high power plasma pulse interacts with a surface for a short time, followed by a long off period, where relaxation may occur and/or neutral species may still adsorb.

The connection between ion bombardment and structure evolution is studied for many PVD systems. For the case of alumina, Andersson et al showed that a variation of the oxygen partial pressure leads to a change in the dc self-bias at the target, thus to a different ion bombardment and finally to a different crystallinity of the films [4]. In such experiments, however, many parameters are changed simultaneously, so that one may always object that other factors such as the different plasma chemistry and surface coverages of oxygen may influence the structure evolution as well.

In this paper, we resolve this ambiguity in the interpretation of the experiments by devising an approach, where we keep the average energy per deposited atom (E), the average energy of the incident ions (Eions), the total ion flux (Jions), and the ion-to-neutral ratio (Jions/Jgrowth) constant, but changing only the IED. This is realized using an rf-magnetron to maintain a constant plasma background assuring a constant stream of neutrals (Jgrowth) and ions (Jions) towards the substrate. At substrate level, variable biasing is applied to modulate the energy and temporal distribution of the ions impinging on the substrate (IED).

This experimental approach can be applied in principle to any material system. Here, we selected aluminum oxide (Al2O3) as a prominent material with applications ranging from microelectronics, wear resistant coatings to catalytic surfaces [5]. The most common phases of Al2O3 are the γ and α phase. α-Al2O3 with its hexagonal closed package (hcp) [6] structure is often used as hard coating on machining tools. The metastable γ-Al2O3 phase [7] exhibits low surface energy making it most suitable as absorbent or as catalyst [8].

In a review published by Levin and Brandon et al [8] the transition temperatures for bulk alumina processing from boehmite to γ-alumina are in the range 300–500 °C. The transition from γ-alumina to the δ phase occurs at temperatures between 700 and 800 °C. The broad range of transition temperatures reflects the experimental fact that differences in the precursors used for alumina synthesis impact the transition temperature. It is known that these thermodynamical transition temperatures can be lowered by applying an additional ion bombardment.

Edlmayer et al [9] deposited films at 640 °C and annealed them afterwards. They observe a bulk diffusion induced transition to γ-alumina at 800 °C. Musil et al [10] reported a 200 °C larger transition temperature to γ-alumina than Edlmayer et al [9] for nanocrystalline γ-alumina thin films. This may be understood by considering bulk transition data reported by McHale et al [11] and thin film transition data reported by Rosén et al [12]: the lower surface energy of γ-alumina as compared with α-alumina, thermodynamically stabilizes the γ phase relative to the α phase. The enhanced thermal stability of the γ-alumina coatings observed by Musil et al [10] may be caused by the smaller grain size (nanocrystallinity) of the as-deposited γ-alumina coatings.

This allows that the transition temperatures to γ-alumina are very sensitive to the preparation conditions and may, therefore, serve as an excellent monitor signal for the ion-induced effects plasma deposition.

2. Experimental methods

2.1. Film deposition

Deposition is performed using a two frequency rf-magnetron sputter experiment (see figure 1, for more details see [13]). Hall probe measurements have shown that the inner magnetic field density is higher than the outer magnets. According to Window et al [14], this magnetic configuration refers to a magnetic configuration from type I. The target consists of 99.99% pure aluminum and has a diameter of 140 mm. The plasma is powered with 300 W at 71 MHz and with 200 W at 13.56 MHz. A broadband amplifier is used to power the electrode with a sinusoidal signal of 71 MHz, matched by a matchbox from Aurion (see figure 1). The second frequency is applied by a Dressler Cesar (Model 136) at 13.56 MHz. Both frequencies are directly coupled to the target electrode. The high frequency at 71 MHz supports a high plasma density, whereas the low frequency of 13.56 MHz adjust the bias potential at the target and thereby the energy of the sputtering ions.

![Figure 1. Magnetron sputter setup with the powered electrode where both plasma generator devices are shown. Above an aluminum target, a magnet configuration is located. On the opposite site, the substrate electrode is installed, which can be heated and powered by an arbitrary biasing signal.](image-url)
An argon discharge is generated at a pressure of 0.1 Pa, using a constant argon flow rate of 9 sccm. A feedback loop regulates the oxygen flow into the chamber avoiding target poisoning. The feedback loop is based on maintaining a constant intensity of the Al I emission line at 396.2 nm, measured by a photomultiplier. Thereby, stoichiometric correct Al₂O₃ coatings are prepared as being verified by an elemental analysis using x-ray photoelectron spectroscopy.

The distance between the target and the Si(1 0 0) p-doped substrate is 50 mm. The substrate is heated during the deposition process to a temperature of 500 °C, 550 °C and 600 °C, respectively. Before starting any deposition, the temperature of the hot substrate is controlled by measuring the temperature dependent refraction index of silicon at 632.8 nm by ellipsometry [15]. This method is non-intrusive and measures directly the surface temperature. Alternatively, pyrometry can be used in principle, but the results may remain ambiguous because the emissivity of the coated silicon wafer is not well defined and silicon becomes transparent in the infrared wavelength range at high temperatures.

The easiest and most accurate way to measure temperatures is the use of a thermocouple. However, such a method is not easily applicable in our experiment: first, the substrate is inserted into the chamber via load lock system. Good thermal contact of a thermocouple with the substrate holder is possible, but it is difficult to realize a good contact with the moveable substrate itself. Therefore, a possible temperature difference between holder and substrate may remain undetected. Second, the substrate electrode (also the substrate itself) is biased by an rf signal with an amplitude of 100 V and more, which couples capacitively (also the substrate itself) is biased by an rf signal with an amplitude of 100 V and more, which couples capacitively onto the meV thermocouple signal inducing a large systematic error. Therefore, an optical method to monitor substrate temperatures is preferred as it is standard in semiconductor plasma processing.

2.2. Substrate biasing

The substrate electrode is biased with rectangular waveforms with varying amplitudes \( V_{\text{max}} \) and frequencies \( f \) between 1.01 and 1.40 MHz. At this frequency, the ions can still follow the modulation of the sheath voltage so that ions entering the sheath experience the full potential drop between sheath edge and surface. The bias signal at the substrate electrode is recorded by a VI probe in the rf feed line. In addition, the dc self-bias \( V_{\text{dc}} \) is recorded by low-pass filtering of the rf signal at the substrate electrode. The deposition is performed using three different rectangular bias waveforms. By adjusting the power of the substrate bias, the dc-self-bias varies as well. The parameters are adjusted in a manner so that the average energy of the incident ions \( E_{\text{ions}} \) remains identical irrespective of the chosen frequency \( f \).

The biasing parameters are directly defining the energy distribution of the incident ions and thereby also the average energy of the ions. The ion velocity distribution (IVD), from which the IED can be calculated easily, has been measured by a retarding field analyser (RFA) in a pure argon discharge and is being compared with a simple analytical [16] as well as numerical model [17]. Perfect agreement has been found. Due to the low pressures, all sheaths can be considered collisionless, and the bias waveform can be directly converted into an IED. This direct conversion of the bias waveform into an IED has the great advantage that an IED can be also estimated for experimental conditions, where a direct RFA measurement is not possible. In the case of Al₂O₃ deposition, the substrate is heated and any Al₂O₃ coating will also create insulating films inside the RFA, making a direct measurement impossible. Since the majority of the ions in our plasma consists of argon, the estimate of the IED from the data of a pure argon plasma is reasonable.

To connect the bias waveform to the sheath voltage and thus to the IED, two cases need to be distinguished [18]: (i) if the bias voltage is lower than the floating potential, the sheath voltage corresponds to the difference between the bias voltage measured by the VI probe and the plasma potential \( \nu_{\text{plasma}} = 18 \text{ V} \) in our case as being determined by Langmuir probe; (ii) if the voltage becomes too positive, it pushes the plasma potential even higher. In this case, the voltage drop remains constant and it corresponds to only the difference between plasma potential and floating potential, yielding a constant voltage drop of 14 V.

The connection between the temporal evolution of the sheath voltage as derived from the VI data and the IED has been modelled even in greater detail by Shihab and Brinkmann [17]. A self-consistent plasma sheath model has been developed for arbitrary substrate signals including also ion inertia. This goes beyond traditional sheath models, which are usually limited to a certain bias frequency regime. Details of this model are presented elsewhere [17]. The input parameter for that model are oscilloscope data representing the bias signal at the substrate electrode. Because most of the produced ions in the plasma are argon ions, we assume \( m_i = 40 \text{ amu} \). Semmler et al [19] measured the electron temperature with an automated probe system (APS3) fully automated Langmuir probe using this setup under similar conditions. Regarding these measurements, we expect an electron temperature of \( T_e = 4 \text{ eV} \). The mean energy \( \langle E \rangle \) is calculated from the modelled IED. The connection between arbitrary waveforms and the IEDF could be verified by Baloniak et al [20] by measuring the IVDF with a RFA and fitting this distribution to the entitled models.

The absolute ion fluxes are determined by measuring the electron density in front of the substrate under deposition conditions, using a plasma absorption probe (PAP) [21]. The tip of the probe is mounted at a distance of 23 mm to the target. In the centre above the target an electron density of \( n_e = 5.8 \times 10^{16} \text{ m}^{-3} \) is determined. By applying the Bohm criterion an absolute ion flux of \( J_{\text{ions}} = 13.5 \times 10^{18} \text{ m}^{-2} \text{s}^{-1} \) is determined. This is compared with the flux of incorporated species as derived from the growth rate. This yields a constant ion-to-neutral flux ratio in our experiment of \( J_{\text{ions}}/J_{\text{growth}} = 0.24 \).

2.3. Thin film analysis

The aluminum oxide films are analyzed by Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and profilometry.
Ex situ FTIR transmission measurements of the sample are performed at 60° angle of incidence using a Bruker IFS 66/S spectrometer in the wavenumber range between 400 and 6000 cm$^{-1}$. Non-coated silicon wafers are used to take the background spectra. The infrared spectra are compared with a model for the optical constants established by Chu et al [22]. According to that model, the optical dielectric function of aluminum oxide is composed of a series of classical Lorentz oscillators:

$$
e_2(\omega) = \epsilon_\infty + \sum_n \frac{S_n \omega_n^2}{\omega_n^2 - \omega^2 - i \omega \gamma_n},$$

(1)

where $S_n$ is the strength of the oscillation, $\omega_n^2$ the wavenumber of the transversal oscillation, $\omega_n^2$ the wavenumber for the longitudinal oscillation and $\gamma$ the damping factor. $\epsilon_\infty$ describes the contribution of the optical transitions outside the infrared spectral range. Each oscillator consists of a longitudinal and a transversal oscillation. According to this description, crystalline $\gamma$-alumina can be identified by a pronounced peak at 950 cm$^{-1}$ corresponding to the LO phonon [23]. Amorphous alumina layers exhibit a rather featureless absorption spectrum. Equation (1) has been used to devise an optical model of the thin films on silicon wafers to simulate the infrared transmission spectra.

Structural analysis was carried out by XRD using a Bruker D8 General Area Detection Diffraction System (GADDS) with Cu Kα radiation at an incident angle of 15°. The analyzed 2θ range was 20°–70°. The applied voltage and current settings were 40 kV and 40 mA, respectively.

Finally, film thickness has been measured by profilometry. From the known density of alumina, the flux $J_{\text{growth}}$ of incorporated atoms during the deposition time can be calculated.

3. Results

3.1. Variation of the IVDF

Film deposition has been performed at constant plasma parameters of 200 W at 13.56 MHz and 300 W at 71 MHz, but varying bias signal at the substrate electrode. This variation is performed using a rectangular pulsed bias with different maximum voltages $V_{\text{max}}$ and frequencies $f$. The rectangular bias consists of two phases, the time $\tau_{\text{on}}$ when the bias is applied and $\tau_{\text{off}}$ when the substrate is at floating potential. The duty cycle (d.c.) corresponds to $\tau_{\text{on}}/(\tau_{\text{on}} + \tau_{\text{off}})$ and the frequency $f$ of the biasing to $1/(\tau_{\text{on}} + \tau_{\text{off}})$. Since the total flux of ions and neutrals remains constant, the average energy per deposited atom $\langle E \rangle$ can be calculated as

$$\langle E \rangle = E_{\text{ions,max}} \cdot \frac{J_{\text{ions}}}{J_{\text{growth}}} \cdot \tau_{\text{on}} \cdot f = E_{\text{ions}} \cdot \frac{J_{\text{ions}}}{J_{\text{growth}}}.$$  

(2)

The mean energy $\langle E \rangle$ is calculated from the knowledge of the IVDF tailored by the biasing signal (see section 2.2): first, the IVDF is averaged over one period, yielding the term $E_{\text{ions,max}} \cdot \tau_{\text{on}} \cdot f$. Second, the average energy per incorporated atom, $\langle E \rangle$ is calculated by weighting the average ion energy with the ratio of ion fluxes to growth flux $J_{\text{ions}}/J_{\text{growth}}$.

The growth flux $J_{\text{growth}}$ is calculated from the growth rate of the films. The film thickness is kept constant at 1 µm for each sample to ensure a good comparability between the samples. This thickness results in a deposition rate of $(0.52 \pm 0.09)$ nm s$^{-1}$ for all samples. This equation indicates that an identical parameter $\langle E \rangle$ can be obtained for identical values of $J_{\text{ions}}/J_{\text{growth}}$ and $\tau_{\text{on}}$ in the growth flux by simultaneously changing $E_{\text{ions,max}}$ and $f$. Since we kept the
The different biasing concepts lead to different IEDs, as shown in figure 2. One can clearly identify the bi-modal structure of the distribution functions. Due to the low pressure, any enhancement of the low energy part is almost negligible, and due to the low frequency of the bias in the range of only \( f = 1–1.40 \) MHz, the actual applied voltage almost directly transfers to the energy of the incident ion. The inertia of the ions leading to an averaging of the sheath energies becomes only significant for higher frequencies. One can clearly see that the IVD changes in a very characteristic manner see figure 3. For low d.c. or low frequencies, the maximum energy of the ions is higher, but their contribution to the total ion flux is smaller as indicated by the peak height. At higher d.c. it is the reverse. If one averages the IED functions, one obtains in each case an average energy around \( E_{\text{ions}} \approx 55 \) eV. Together with the growth flux, this results in an average energy per deposited atom of approximately \( \langle E \rangle \approx 10–15 \) eV, as calculated from equation (2).

3.2. Connection between IVDF and thin film properties

Alumina films were deposited using three different schemes with identical \( \langle E \rangle \approx 11 \) eV and \( E_{\text{ions}} \approx 55 \) eV, but different maximum ion energies \( E_{\text{ions,max}} \) and duty cycles d.c. or frequencies \( f \). In addition, three different substrate temperatures have been chosen, namely 500 and 550 and \( 600 \) °C. Thereby, the influence of the ion bombardment on the formation of the crystalline \( \gamma \) phase may become visible by a lower transition temperature from the x-ray amorphous to the \( \gamma \) phase.

Since it is well known that H incorporation into growing alumina [24] and strontium titantate thin films [25] affects structure evolution [24, 25] as well as the elastic properties [26] we have taken great care to utilize the lowest residual gas background obtainable with the equipment employed here for synthesis. Since the base pressure after baking was \( 2 \times 10^{-5} \) Pa, we expect a water condensation rate below \( 0.01 \) nm s\(^{-1} \) which is expected to result in a H incorporation of significantly \(<2\) at\% [26]. The effect of this comparatively small incorporation of H on the phase stability is beyond the scope of this work.

The deposited films were analyzed by FTIR spectroscopy, as shown in figure 4. All films, deposited at \( 600 \) °C show a pronounced feature at \( 950 \) cm\(^{-1} \) indicating the LO absorption of \( \gamma\)-Al\(_2\)O\(_3\), being characteristic for \( \gamma \)-crystalline films showing that the alumina films grow in the thermodynamically preferred \( \gamma \) phase, irrespective of the biasing scheme. The sharp peak at \( 950 \) cm\(^{-1} \) is much less pronounced in the spectra of all other films, except the films deposited at a frequency of \( f = 1.20 \) MHz at \( 550 \) °C. All FTIR spectra are modelled using four oscillators described by equation (1). A good agreement between model and measured spectrum can be found, shown for a sample with \( 1.01 \) MHz bias and \( 600 \) °C in figure 4(a), bottom.

XRD analysis was performed to investigate the phase formation of the as-deposited Al\(_2\)O\(_3\) thin films as a function of the frequency and substrate temperature (figure 5). As can be seen, the sample deposited at \( 600 \) °C (figure 5(b)) exhibits small peaks at 45.86° and 67.03° which correspond

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**Figure 3.** Ion velocity distribution function for three parameter sets: (a) \( f = 1.01 \) MHz and \( E_{\text{ions,max}} = 120 \) eV; (b) \( f = 1.20 \) MHz and \( E_{\text{ions,max}} = 100 \) eV; (c) \( f = 1.40 \) MHz and \( E_{\text{ions,max}} = 80 \) eV.

fluence of energetic ions \( J_{\text{ions}} \cdot t_{\text{on}} \) also constant during one pulse \( t_{\text{on}} = 0.5 \mu s \), we only varied \( t_{\text{off}} \) and thereby \( f \). The corresponding variation of the substrate bias signal for three frequencies \( f \) are shown in figure 2. It can be seen that the maximum negative voltage \( V_{\text{max}} \) at the substrate electrode is simultaneously changed with \( t_{\text{off}} \), by adjusting the power of the biasing system for a given frequency \( f \).

The different biasing concepts lead to different IEDs, as being modelled using the very same \( V(t) \) curves as shown
to the (4 0 0) and (4 4 0) direction of γ-Al2O3 at a substrate temperature of 500 °C. The samples deposited at a frequency of 1.01 MHz (figure 5(a)) and 1.40 MHz (figure 5(c)) appear to be x-ray amorphous at 500 °C. As the substrate temperature is increased to 550 and 600 °C the increased diffraction peak intensities indicate improved crystal quality of the Al2O3 thin films deposited at 1.01 and 1.20 MHz, while the sample deposited at 1.40 MHz exhibits a relative weak peak at 45.86° for a substrate temperature of 550 °C which is also assigned to the (4 0 0) direction of γ-Al2O3. With a further increase in substrate temperature to 600 °C an additional γ-Al2O3 peak at 67.03° and a distinct increase of peak intensity is observed.

4. Discussion

The thin film analysis revealed that the biasing scheme at \( f = 1.20 \text{ MHz} \) leads to the growth of γ-alumina already at 500 °C or slightly above, which is significantly lower than any temperature for \( f = 1.01 \text{ MHz} \) or \( f = 1.40 \text{ MHz} \) bias, where crystallinity is reached. This raises the question about the peculiar nature of the deposition parameters \( f = 1.20 \text{ MHz} \) and \( E_{\text{ons,max}} = 100 \text{ eV} \). The flux of neutrals and of ions is \( J_{\text{growth}} = 56.1 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1} \) and \( J_{\text{ions}} = 13.5 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1} \), respectively. The three biasing schemes are different in two aspects, namely the different off times \( \tau_{\text{off}} \) and the different maximum ion energies \( E_{\text{ions,max}} \).

The possible influence of both parameters on the growth process is discussed in the following:

- **Influence of \( \tau_{\text{off}} \):** The different off times \( \tau_{\text{off}} \) may correspond to different time spans for the material to relax into a crystalline structure in between the periods during \( \tau_{\text{on}} \) when energetic ions impact on the surface. One may speculate that the adsorbing neutrals require an appropriate time to reach a preferred crystalline adsorption site. If an incident ion impacts on the surface, the motion of the neutral adsorbing atoms may be disturbed and crystal formation is thus prevented. The total time span of a pulse is of the order of 1 µs, resulting in a fluence per pulse of neutral and of ionic species of \( 10^3 \text{ cm}^{-2} \). If one compares this fluence with the typical number of surface...
Figure 5. X-ray diffraction spectra for films deposited at three different substrate temperatures and different biasing schemes: (a) $f = 1.01$ MHz and $E_{\text{ions, max}} = 120$ eV; (b) $f = 1.20$ MHz and $E_{\text{ions, max}} = 100$ eV; (c) $f = 1.40$ MHz and $E_{\text{ions, max}} = 80$ eV. The average energy per incorporated atom $\langle E \rangle$ is equivalent to 11 eV. The average ion energy $E_{\text{ions}} \approx 55$ eV.

sites of $10^{15}$ cm$^{-2}$, one can conclude that the ions and neutrals impact the surface well apart from each other of the order of 1000 lattice sites equivalent to 30 nm. Any mutual and simultaneous reaction of neutrals and ions might only occur, if either the lateral size of the collision cascade or the travel distance of the neutrals within 1 $\mu$s via surface diffusion is larger than these 1000 lattice sites as the average distance in between the impacting species. The adsorbed neutrals may diffuse on the growing film surface during the time span of a 1 $\mu$s pulse. If one assumes a minimum activation barrier for surface diffusion of 1.6 eV as reported for $\alpha$-Al$_2$O$_3$ [27], the adsorbed neutrals are estimated to diffuse a few nanometres within a 1 $\mu$s pulse. This may be compared with the surface regions that are affected by the collision cascades of the incident ions. TRIM simulations reveal that the lateral size of the collision cascade for argon ions with an energy of a few 100 eV is also only of the order of a few nanometres. Consequently, the impact of neutrals and of ions during one d.c. are isolated events well apart at the growing film surface. One may consider these events, therefore, uncorrelated and any detailed influence of the timing of the off time can thereby be excluded.

- **Influence of $E_{\text{ions, max}}$:** The different maximum ion energies result also in different collision effects upon impact at the growing film surface. To quantify the ion-induced effects, we performed TRIM calculations to assess the energy dissipation of the incident argon ions during thin film growth in the energy range between 30 and 100 eV. The bulk binding energies, displacement energies and surface binding energies are taken from [28]. The displacements per incident ions and depth interval of 0.2 nm are plotted for various energies together with the implantation profile of 100 eV argon ions in figure 6. One can see that the displacements per ions increase with energy and reach a value of 0.8 per incident ion and 0.2 nm depth interval at the film surface at an energy of 100 eV. In total, one surface atom is displaced by an incident argon ion at 100 eV within the penetration depth of the incoming ions. The ion-to-neutral during film growth is 1/5. One may argue that the displacement of one surface bonded atom causes the re-arrangement of this
atom including also its next neighbours. Additionally, an optimum ratio between displacements per ion and the activation of surface atoms appears to be reached at an Ar ion energy of 100 eV. Larger ion energies may result in resputtering while lower energies result in a reduced number of displacements per ions and hence a reduced adatom mobility. Thereby, the displacement events at the growing film surface being proportional to $J_{\text{ions}}$ are able to affect all incorporated atoms during film growth given by $E_{\text{growth}}$.

The present experiments are also consistent with other findings on the influence of the collision cascades on thin film growth. Music et al. [29] used molecular dynamics simulations to show that the transition of $\gamma$-alumina to $\alpha$-alumina may be promoted by subplantation of bonded atoms only once in average to favour the transition of $\gamma$-alumina to $\alpha$-alumina may be promoted by subplantation of the incident ions. This modelling is corroborated by experiments on $\text{Al}_2\text{O}_3$ deposition from a filtered arc, $\text{Ar}$ ion energy of 100 eV. Larger ion energies may result in resputtering while lower energies result in a reduced number of displacements per ions and hence a reduced adatom mobility. Thereby, the displacement events at the growing film surface being proportional to $J_{\text{ions}}$ are able to affect all incorporated atoms during film growth given by $E_{\text{growth}}$.

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Figure 6. Displacements per incident ions and depth interval of 0.2 nm for argon bombardment of $\text{Al}_2\text{O}_3$ (solid symbol). Implantation of 100 eV argon ions in $\text{Al}_2\text{O}_3$ (open symbols).

Summarizing, one may conclude that the optimal growth process is designed, if the impacting ions displace the surface bonded atoms only once in average to favour the transition from an amorphous to the crystalline $\gamma$-alumina structure at a reduced substrate temperature. One may speculate that displacements events are too few, if the energy $E_{\text{ions,max}}$ is significantly below 100 eV and the structure is, therefore, unable to reach its crystalline state. In contrast, if the energy $E_{\text{ions,max}}$ is well above 100 eV, too many displacement events per incorporated atom occur and the induced damage apparently prevents the formation of any crystalline material. This hypothesis is consistent with the findings of Petrov et al. [2] for titanium nitride deposition, who concluded that either an energy of around 20 eV is essential to promote the enhancement of adatom mobility or energies above 50 eV to promote forward sputtering and a densification of the material.

In the case of $\gamma$-alumina, the preferred energy is rather 100 eV indicating that the one time displacement of each incorporated atom plays the dominant role in the formation of $\gamma$-alumina films.

5. Conclusion

$\text{Al}_2\text{O}_3$ films were deposited by reactive magnetron sputtering using arbitrary substrate biasing. By choosing a rectangular bias with varying frequency and varying maximum voltage an experiment is devised where the average ion energy, the average energy per incorporated atom and the fluxes of ions and neutrals remain constant. Only the ion velocity distribution (IVD) is varied. We observed a reduction in the substrate temperature necessary for the formation of $\gamma$-alumina films from 600 °C to almost 500 °C for a frequency of the rectangular biasing of 1.20 MHz, with a resulting rather mono-energetic ion energy distribution of the ions impacting on the surface with $E_{\text{ions,max}} \simeq 100$ eV. Based on TRIM calculations, this corresponds to a situation, where each surface bond atom is rearranged exactly one time during film growth which apparently promotes the formation of $\gamma$-alumina films.

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