Electron Irradiation Effects in Au thin Films

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Electron irradiation effects in Au thin films

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Abstract Room temperature 200 keV electron irradiation effects on the area retraction behavior presented by 6.75 nm thick Au thin films deposited over a self-standing SiO₂ / silicon nitride membrane are investigated as a function of the irradiation fluence Φ . The as-deposited films already contain void discontinuities. The void growth behavior is investigated considering irradiation and thermally-induced surface atoms' migration. The film's coverage area $A(\Phi)$ and void perimeter $P(\Phi)$, obtained via Transmission Electron Microscopy observations, allow for calculating the atomic displacement causing the area retraction. This data is compared with model calculations of irradiation and thermally-induced atomic fluxes. The results demonstrate that the balance between the thermal and irradiation processes strongly depends on the choice of the surface thermal diffusivity values, which present large discrepancies in the literature. Our results suggest that irradiation-induced atomic displacements follow the same thermodynamic driving forces acting in thermal processes. The work also discloses a new method to investigate surface atoms' behavior and promote microstructural modifications at room or lower temperatures.

Keywords Au thin films · electron irradiation · atomic displacement

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1 Introduction

Thin films and other nanoscopic objects are thermodynamically unstable structures. Upon heating, thin metallic films deposited over a solid substrate may follow a solid-state edge retraction process (also referred to as solid-state dewetting) at temperatures much lower than the corresponding bulk material melting point [1–4]. Due to a smaller migration enthalpy, the diffusion of interface located atoms (e.g., free surfaces and grain boundaries) controls the dewetting process driven by the free interface energy minimization. In general, dewetting renders percolated nanostructures and particle arrays forming at the later stage [2–4]. Dewetting is mostly a degradation mechanism. In thin films for device application, it imposes an operating temperature limit. Through dewetting, however, it is also possible to explore the change in physical properties appearing within the dewetting percolation threshold [5–7] and produce complex systems including, for example, arrays of nanoparticles [3, 8, 9], nanowires [10], and some ordered structures [4, 8, 11].

Nano-objects have a large fraction of their constituent atoms located at interfaces, and this fraction increases with the decrease of the nano-object volume. As compared to fully coordinated bulk atoms, the interface atoms present an imbalance on bond strength, number of bonds, and relative lattice positions that weaken their binding energy [12, 13]. This weakening effect is more pronounced at interfaces presenting a small curvature radius, being phenomenologically described by size-dependent melting temperature or cohesion energy approaches [14, 15]. The binding condition of interface atoms may also influence the nano-objects structural stability against irradiation-induced atomic displacements. Atoms are displaced when the transferred energy is equal or larger to a given threshold displacement energy E_d . Electron irradiation provides a remarkable tool to investigate this phenomenon, especially for metallic materials where irradiation-induced damage results from elastic binary-collision events [12]. Multiple collisions [16], excessive sample heating [17], and bulk atom displacements can be avoided by adequately adjusting the sample thickness and the irradiation parameters energy and flux. This adjustment renders single atom displacement per electron, and the collision is uncorrelated in space and time concerning a second electron impact in the same sample region.

Consequently, through electron irradiation experiments, the displacement rate enhancement of interface located atoms allow shape, size, and object position modifications at lower temperatures than those

required by thermally activated processes. For example, *in-situ* transmission electron microscopy experiments show that the irradiation-induced displacement of Si and O atoms at the nanoparticle-matrix interface significantly enhances the Brownian-like migration of liquid Pb nanoparticles (NPs) embedded in a silica thin film heated at 1100°C [18]. Room temperature electron-irradiations also lead to noticeable microstructure modifications. Irradiations in 100 nm thick silicon nitride self-standing membranes implanted with Au ions produce Au NPs at the electron beam exit surface [19]. The Au NPs are formed according to the following arguments: i) the irradiation causes the sputtering of Si and N atoms from the membrane, exposing the implanted Au content to the free surface; ii) it promotes the migration of the surface-located Au atoms; iii) the formation of Au-Au atomic bonds minimizes the system free energy causing the formation of NPs presenting semi-spherical shapes to reduce the particle interface energy. Electron irradiation experiments can also explore the binding condition of surface atoms. In a recent study considering room temperature electron irradiation of Ag NPs (beam energies from 120 to 200 keV), Konrad et al. [20] demonstrate that the sputtering rate increases as the NP radius r decreases. The study also shows that the observed surface binding energy $E_b(r)$ behavior controlling the sputtering process follows a scaling relation $\frac{E_b(r)}{E_{b_0}} = \frac{E_c(r)}{E_{c_0}}$, being $E_c(r)$ the size-dependent cohesive energy [13, 21, 22], E_{b_0} and E_{c_0} the corresponding binding and cohesive energy values for flat interfaces ($r = \infty$).

A similar scaling relation between $E_c(r)$ and the melting temperature $T_m(r)$ of metal NPs is often considered to validate $E_c(r)$ models using $T_m(r)$ measurements [13, 21–23]. The scaling concept is also generalized to other physical properties derived from the cohesion energy E_c , including, for example, surface diffusivity D_s , Young modulus Y , and Debye temperature θ_D , which can hardly be experimentally evaluated [13, 14, 21, 22]. The scaling relation derived from electron irradiation experiments seems to link electron irradiation- and thermally-induced processes [20]. If a generalized scaling behavior (e.g. $\frac{E_b(r)}{E_{b_0}} = \frac{E_c(r)}{E_{c_0}} = \frac{T_m(r)}{T_{m_0}}$) holds, it should also apply to other nano-objects' size-dependent physical properties and explored via irradiation experiments at room or lower temperatures.

The present study reports on *in-situ* Transmission Electron Microscopy (TEM) observations of Au thin films' edge retraction behavior caused by 200 keV room temperature electron irradiations. We use 6.75 nm thick Au films deposited over a self-standing SiO₂ (15 nm thick) / Si₃N₄ (50 nm thick) membrane. The retraction of the film coverage area allows for the calculation of the corresponding amount

of transported atoms. The study emphasizes the conspicuous behavior of interface atoms, particularly at free interfaces presenting small curvature radius r . We investigate irradiation- and thermally-induced atomic transport processes and demonstrate that their balance is susceptible to small variations (approximately 0.1 eV) in the thermal activation enthalpy barrier values for surface diffusion. It also supports the idea that fine-tuned room temperature electron irradiations preserve thermodynamic driving forces and cause similar target modifications observed in the thermally-induced dewetting process developing at higher temperatures.

2 Experimental procedures

The present experiments were conducted using thin films of Au/SiO₂ deposited by magnetron sputtering at room temperature, using an AJA Orion-8 UHV from the Nanometric Conformation Laboratory, Universidade Federal do Rio Grande do Sul (UFRGS). The Au and SiO₂ depositions were performed onto silicon nitride self-standing membranes (≈ 50 nm thick) supported by a silicon frame, depicted in Fig. 1(a). Fig. 1(b) shows a Rutherford Backscattering Spectrometry (RBS) measurement using a 1.2 MeV He⁺ micro-beam ($\approx 107 \mu\text{m} \times 62 \mu\text{m}$) with a current intensity of 900 pA (micro-beam line, Ion Implantation Laboratory, UFRGS). The RBS measurement, fitted using the SIMNRA simulation code [24], renders the determination of the samples' N, O, Si, and Au content (indicated in the figure). The measured atomic content provides the film thickness estimations shown in Fig. 1(a). The electron irradiation, conducted with a 200 keV beam and a current density of $27 \text{ A}\cdot\text{cm}^{-2}$, was performed using a JEM 2010 transmission electron microscope equipped with a LaB₆ filament, operating at the magnification of 6×10^5 times (Microscopy and Microanalysis Center - UFRGS). Figure 1(a) also depicts the electron irradiation direction, being the Au film at the electron beam exit surface. The beam current is determined by calibrations using a Faraday cup from a low background Gatan holder. At certain time intervals, the beam current density and the magnification are decreased to proceed with microstructure characterization. A detailed record of the irradiation time and beam current density values determines the irradiation fluence Φ (further expressed in electrons nm^{-2}).

Fig. 1 (a) Schematic cross-section view of the samples. Notice the layer description, thickness information, and the electron irradiation direction indication; (b) Rutherford Backscattering measurement. The continuous lines denote a SIMNRA [24] simulation fit through the experimental points. The legends inform the detected atomic content.

3 Results and characterization

Figure 2(a) shows bright-field (diffraction contrast) TEM micrographs depicting the as-deposited film (left side) and the modified structure after irradiation to an accumulated fluence $\Phi = 2.9 \times 10^{10} \text{ e}^- \text{ nm}^{-2}$ (right side). The left and right sides of the selected area diffraction (SAD) patterns in Fig. 2(b) correlate with the corresponding images in Fig. 2(a). Although a significant shape transformation from a discontinuous film towards a percolated arrangement of rod-like structures occurs, the polycrystalline organization of Au cubic structure (Fm-3m space group) remains unchanged (see indexed SAD pattern fit).

Figure 3 provides more detailed TEM images of the irradiation-induced morphological changes as a function of Φ . The micrographs are from the same sample area and clearly show that the irradiation process causes an enlargement of the pre-existing film discontinuities, further referred to as voids.

The void growth behavior implies a redistribution of Au atoms from the void edges towards the film's flat area. The void size evolution allows for the computation of the redistributed atomic flux in terms of two observables: the film covered area A and the total void perimeter P . Image processing

Fig. 2 (a) TEM micrographs showing the initial condition of the Au film (left) and the changes produced by an irradiation fluence $\Phi = 2.9 \times 10^{10} \text{ e}^- \text{ nm}^{-2}$ (right); (b) measured SAD ring patterns. The patterns are correlated with the left and right images in (a). Notice the fitted ring pattern using the Au crystallographic parameters.

techniques render a detailed account of A and P values as a function of Φ , illustrated in Fig. 4. This figure shows a TEM micrograph (Fig. 4(a)), the contrast threshold process to characterize the voids (Fig. 4(b)), and the characterization of the voids perimeters (Fig. 4(c)). Notice that the film covered area $A(\Phi) = A_{mg} - \sum_{i=1}^N A_i^\nu(\Phi)$ and the perimeter $P(\Phi) = \sum_{i=1}^N P_i^\nu(\Phi)$ represent integral values. A_{mg} is the micrograph accounted area, A_i^ν and P_i^ν are the area and the perimeter of the i^{th} void. Figure 5 shows $A(\Phi)$ and $P(\Phi)$ values extracted from the image processing method considering the central part of the irradiated region, where the beam intensity distribution is approximately uniform. The continuous lines in Fig. 5 correspond to polynomial fits of $A(\Phi)$ and $P(\Phi)$. At $\Phi = 0$, the calculated amount of deposited Au atoms obtained by RBS measurements and the TEM observed voids' size distribution renders a corrected film thickness $h = 6.75 \text{ nm}$. We notice that $A(\Phi)$ and $P(\Phi)$ vary more abruptly as the irradiation starts and

Fig. 3 TEM micrographs illustrating the films microstructure evolution as a function of the irradiated fluence Φ . Notice the fluence indication in the micrographs and the size indication in the upper left.

Fig. 4 Illustration of the threshold contrast process to determine the void areas and perimeters. (a) original TEM micrograph, the white regions correspond to void images; (b) threshold contrast process to determine the voids areas; and (c) determination of the voids perimeters from the dark structures in (b).

Fig. 5 (a) Film covered area A and (b) the integrated perimeter P of the void structures. A and P are expressed as a function of the irradiation fluence, Φ , and determined using the threshold contrast method illustrated in Fig. 4 (see text). The error bars correspond to the errors in the threshold contrast process. The continuous lines results from a least-square fit optimization using the functions presented in the figure.

then smoothly evolve with Φ . This transient behavior occurs because the atoms quickly re-accommodate from the as-deposit to a more stable configuration.

4 Discussion

Electron irradiation damage in metals results from binary elastic collision events [25]. Figure 6 shows the Rutherford unscreened elastic collision cross-section σ_d for irradiation-induced Au displacements versus the transferred energy, expressed in terms of the displacement threshold energy parameter E_d [12]. The

Fig. 6 Unscreened Rutherford elastic scattering cross-section, σ for 200 keV accelerated electrons impinging into an Au atom. σ is expressed as a function of the transferred energy E_d . The vertical dashed line corresponds to the maximum transferred energy.

cross-section decreases with E_d 's increase and presents a steep variation as E_d approaches the maximum transfer energy ($E_{max} = 2.67$ eV for 200 keV accelerated electrons). The energy necessary to displace a bulk Au atom is $E_{dB} = 34 \pm 7$ eV [26]. The threshold surface binding energy E_s to cause atomic sputtering from a flat surface may present values within $E_{sub} \lesssim E_s \lesssim 5/3 E_{sub}$, being $E_{sub} \approx 3.8$ eV the sublimation energy for bulk Au [12]. Figure 7 shows a void-edge cross-section sketch. According to Konrad et al. [20], the surface binding energy at curved interfaces scales with the local cohesive energy. In terms of the cohesive energy model from Qu et al. [13], the surface binding energy for a surface characterized by a curvature radius r reads

$$E_s(r) \cong E_{s_0} \left(1 - \frac{d}{\eta r} \right), \quad (1)$$

being $E_{s_0} \approx E_{sub} = 3.8$ eV the binding energy of a flat surface, $d = 0.288$ nm the metallic diameter of an Au atom, $\eta = 0.74$ the atomic packing fraction of the FCC Au unit cell, and r the curvature radius of the voids' edge (considered as a circular arc described by a radius $r = h$, being h the film thickness). For $h = 6.75$ nm, Eq. (1) renders $E_s \approx 3.6$ eV. The transferred energies values $E_{max} < E_s(r) < E_s(r = \infty) < E_{dB}$ mean that 200 kV accelerated electrons cannot provide sufficient energy to displace bulk atoms or cause the sputtering of surface atoms, even for those located at the curved film edges. In other words, the observed microstructure modifications during the irradiation experiments

Fig. 7 Schematic cross-section view of a film-void edge presenting an circular-like interface curvature and a segment of the film flat region. The curvature radius r corresponds to the film thickness h . Notice the representation of the possible jump directions at the films edge (p_e) and at the films flat regions (p_f).

have two main characteristics: i) it preserves the atomic Au content; and ii) it results from irradiation and or thermally-induced migration of interface located atoms that require smaller threshold energies for the atomic displacements. To calculate the number of displaced atoms necessary to enlarge the voids, we adopt the following assumptions: i) the atomic flux per unit perimeter length causing enlargement is similar for all voids, regardless of their sizes and shapes; ii) the radius of the voids are larger than the critical radius for the growth process; iii) formation of new voids do not occur; iv) atomic migration at the flat areas of the film is sufficiently fast to keep the film thickness uniform, defined as $h(\Phi) \approx V/A(\Phi)$, being V the total volume of the Au content and $A(\Phi)$ the films' covered area shown in Fig. 5(a). These assumptions render an expression for the atomic flux per unit perimeter, derived in terms of the measured $A(\Phi)$ and $P(\Phi)$ behavior (Fig. 5) as

$$J_{exp}(\Phi) = j \frac{1}{\Omega} \frac{h(\Phi)}{P(\Phi)} \frac{dA(\Phi)}{d\Phi}, \quad (2)$$

being j the beam current density and Ω the atomic volume for metallic Au atoms. To avoid large fluctuations in J_{exp} , we estimate $dA/d\Phi$ using a polynomial fit through the experimental points. The continuous line in Fig. 5(a) represents the fitted $A_{fit}(\Phi)$ function. The evaluation of Eq. (2) also considers a fitted $P_{fit}(\Phi)$ function and $h_{fit}(\Phi) \approx V/A_{fit}(\Phi)$. The error bars on the J_{exp} points account for the errors

Fig. 8 Film coverage area A plotted as a function of the total voids perimeter P . The fitted line corresponds to a function $A(P) = A_{mg} - 2.15 \times 10^{-3} P^2$.

in the evaluation of $A(\Phi)$ and $P(\Phi)$ resulting from the image processing method. The J_{exp} expression is only valid to a limit fluence where a flat film structure presenting large voids still holds (e.g., Fig. 3(f)), and not for large fluences producing a network of interconnected rod-like forms shown in the right side of Fig. 2(a)). Figure 8 shows a plot of $A(\Phi)$ versus $P(\Phi)$. The continuous line represents a parabolic function $A(P) = A_{mg} - 2.15 \times 10^{-3} P^2$. This fit delimits the valid experimental fluence points for the present analysis. The fitted lines in Fig. 5 represent the extent of the fluence range considered in the study, consistently with Fig. 8. $J_{exp}(\Phi)$ represents the atomic flux through a unit perimeter segment and provides a reference to validate model calculations of irradiation- and thermally-induced atomic fluxes (J_{irr} and J_{th} , respectively), considered as uncorrelated processes simultaneously contributing to a total flux $J_{tot} = J_{irr} + J_{th}$.

To estimate the irradiation-induced voids' enlargement flux $J_{irr}(\Phi)$, we make the following assumptions: i) the net surface atomic flux causing the void enlargement occurs through a line demarking the voids' perimeter, separating the curved and the flat areas of the film. The flux parallel to the perimeter line or at the flat surfaces do not contribute to the void enlargements; ii) $\Gamma = j\sigma_d(E_d)$ denotes the atomic jump frequency, being j the beam current density, σ_d the elastic electron-atom collision cross-section (Fig. 6) and E_d the necessary threshold energy to promote the irradiation-induced atomic displacement

at the film surface; iii) the threshold energy E_d follows the same scaling behavior $\frac{E_d(r)}{E_{d0}} = \frac{E_b(r)}{E_{b0}} = \frac{E_c(r)}{E_{c0}}$ discussed in the literature for distinct physical properties [20, 22]. Based on these assumptions, the irradiation-induced atomic flux across a unit perimeter length reads

$$J_{irr} = j\rho_s\alpha\Delta\Gamma. \quad (3)$$

In this equation, ρ_s is the films' surface atomic concentration, α is the atomic jump length in the Au lattice, and $\Delta\Gamma$ the jump rate difference across the perimeter line expressed considering assumption (ii). This approximation renders an overall expression

$$J_{irr}(\Phi) = j\rho_s\alpha[p_e\sigma_d(E_d(h(\Phi))) - p_f\sigma_d(E_{d0})], \quad (4)$$

being p_e the atomic jump probability at the void edge, p_f the jump probability at the flat surface, E_{d0} the atomic displacement energy of a flat surface, and $E_d(h(\Phi))$ the displacement energy at the film-void edge presenting a curvature radius $r = h(\Phi)$. Notice that the incoming electrons are impinging the film in a direction perpendicular to the film's flat surface (see Fig. 7). Hence, the transferred momentum (low impact-parameter collisions) causing the atomic displacement is parallel to the electron incidence direction. Since sputtering events do not occur, the impinged atom must vibrate perpendicular to the film's surface. Due to anharmonic interactions with neighbor atoms, the vibration eventually causes a lateral jump along the surface, rendering a jump probability $p_f \lesssim 1/4$ (Eq. (4)). At the film-void edges, however, the situation can be different. The collision-induced atomic vibration direction is not perpendicular to the edge surface. We are not sure what are the jump probabilities in this situation. Therefore, as an approximation, two simplifying hypotheses for p_e are considered. First, the interactions with neighbor atoms smear-out the vibration direction, rendering a jump probability $p_e \lesssim 1/4$. Second, the vibration direction favors the atomic jump toward the film's flat area, leading to $p_e \lesssim 1/3$, as sketched in Fig. 7. To account for the film's curvature effect, we assume that a scaling relation $\frac{E_d(r)}{E_{d0}} = \frac{E_c(r)}{E_{c0}}$ holds, being $E_c(r)$ the curvature dependent cohesion energy evaluated according to the distinct literature models listed in Table 1. In the following calculations, we will assume that $p_e = 1/3$ and $p_f = 1/4$, which will render upper limit values for the parameter E_{d0} to be determined.

Table 1 Size dependent displacement energies (adapted from the quoted Refs).

Ref.	Authors	Equation	Parameters
[13]	Qu et al.	$E_d(r) = E_{d0} \left[1 - \frac{d}{\eta r} \right]$	$d = 0.288 \text{ nm}$
[21]	Qi et al.	$E_d(r) = E_{d0} \left[1 - \frac{d}{2r} \right]$	$\eta = 0.74$
[22]	Yu et al.	$E_d(r) = E_{d0} \left[\left(\frac{\rho_0}{\rho_p} \right)^{2/3} - \frac{d\rho_0}{2\rho_p\eta r} \right]$	$\frac{\rho_0}{\rho_p} \approx 1$

To estimate the thermal contribution to void edge retraction, we consider a thermal flux expressed as [1, 27]

$$J_{th}(t(\Phi)) = -\frac{D_s \Omega \gamma \rho_s}{k_B T} \nabla_s \kappa, \quad (5)$$

being D_s the surface diffusivity, ρ_s , Ω and h have the same meaning as in the previous equations, k_B is the Boltzmann constant, T is the absolute temperature, γ is the free surface energy. $\nabla_s \kappa$ is the gradient of the interface curvature along the path s . In the present analysis, we assume that a circular arc describes the film-void edge cross-section, being the curvature radius $r = h$. Hence, the interface curvature is $\kappa = 1/r$, and the atomic jumps occur through an arc length $ds = 2\pi dr$, rendering $\nabla_s \kappa = -1/(2\pi r^2)$. The curvature assumption represents a first-order approximation to simplify the calculations [28]. It also implies that the film-edge retraction is estimated disregarding the formation of a rim structure along the edge perimeter, as commonly assumed for thermally activated processes on thicker films [1]. Table 2 shows the values of the physical parameters used in Eqs. (4) and (5). Concerning the D_s values, it is worth to remark that predictions for the Au surface diffusion coefficient $D_s(T) = D_0 \exp(-E_m/k_B T)$ are controversial. Grazyna and Ehrlich [29] present a compilation of the factor D_0 and the migration enthalpy E_m values obtained from the literature. The quoted values for D_0 vary by a factor of 10^6 , and the values for the migration enthalpy range within $0.1 \lesssim E_m \lesssim 1.4 \text{ eV}$. More recently, Niekiet et al. [2] and Müller et al. [30] conducted thermally-induced dewetting studies ($T > 570 \text{ K}$) in Au thin films with distinct thicknesses ($15 \lesssim h \lesssim 35 \text{ nm}$). These authors indicate that the activation energy for the dewetting process varies within the interval $1 < E_a < 1.42 \text{ eV}$, comparing the E_a values with the activation energy for surface thermal migration estimated by Göbel and Blanckenhagen [31], Beszeda et al. [32], Jiran and Thompson [33] and Sanders and DePristo [34]. Our J_{th} calculations (Eq. (5)) will explore the D_s values provided by the above references. Table 3 summarizes the D_s parameters D_0 and E_m obtained from Refs. [31–34], reporting the temperature range of the measurements and the corresponding $D_s(T = 300 \text{ K})$

Table 2 Values of the parameters used in the calculations.

Definition	Symbol	Value
Beam current density	j	$1.685 \times 10^6 \text{ e}^- \text{ nm}^{-2} \text{ s}^{-1}$
Accounted micrography area	A_{mg}	$3.344 \times 10^4 \text{ nm}^2$
Volume of deposited Au / A_{mg}	V	$1.870 \times 10^5 \text{ nm}^3$
Atomic volume (Au)	Ω	$1.69 \times 10^{-2} \text{ nm}^3$
Atomic jump length (Au)	α	0.28 nm
Surface atomic density (Au)	ρ_s	11.46 at.nm^{-2}
Free surface energy	γ	8.115 eV nm^{-2}

Table 3 Surface diffusion coefficient parameters.

Ref.	Authors	$D_0 \text{ (nm}^2\text{s}^{-1}\text{)}$	$E_m \text{ (eV)}$	Temperature range (K)	$D_s \text{ (300 K) (nm}^2\text{s}^{-1}\text{)}$
[31]	Göbel and Blanckenhagen	5×10^6	0.4	300 – 773	0.95
[32]	Beszeda et al.	3×10^7	0.64	573 – 843	5.3×10^{-4}
[33]	Jiran and Thompson	4×10^{12}	1.2	1023 – 1098	2.77×10^{-8}
[34]	Sanders and DePristo	4.9×10^{11}	0.67	400 – 2000 (theory)	2.72

values for each case. Figure 9(a) presents the atomic fluxes J_{exp} (Eq. (2)) and J_{th} (Eq. (5)) for $T = 300$ K. The calculations use the distinct D_s values from Table 3. The J_{th} obtained using D_s values from Refs. [32, 33] are negligible, very probable because extrapolation of D_s to room temperature is not valid (see temperature ranges in Table 3).

On the other side, the D_s parameters from Ref. [34] overestimate the J_{exp} points significantly, suggesting that the Au film is unstable at room temperature, contradicting the experimental results. Finally, the D_s parameters from Göbel and Blanckenhagen [31] lead to a J_{th} contribution of about $1.07 J_{exp}$, also suggesting that the film's stability is susceptible to room temperature fluctuations. Assuming that our calculation approach is consistent, the results indicate that the D_s values obtained from Ref. [31] are slightly overestimated, even disregarding beam heating effects. Electron irradiation-induced temperature increase is difficult to determine. Using the temperature elevation model from Kohl and Reimer [35], we estimate a temperature increase of $\Delta T \approx 1.3$ K for heat drain through the Au film, $\Delta T \approx 4.3$ K if the drain occurs via the silicon nitride membrane, and $\Delta T \approx 9.3$ K if it is done via the silica layer.

Fig. 9 (a) Thermally-induced atomic flux, J_{th} (Eq. (5)) as a function of the irradiation fluence, Φ (continuous lines). The calculated curves are for $T = 300$ K and corresponds to the surface diffusivity parameters listed in Table 3. The square points represent the J_{exp} values (Eq. (2)), calculated using $p_e = 1/3$ and $E_d(r)$ according to Ref. [22]. (b) J_{th}/J_{exp} ratio expressed as a function of the temperature T . The calculations considers $D_0 = 5 \times 10^6 \text{ nm}^2 \cdot \text{s}^{-1}$ and distinct migration enthalpy E_m values from 0.4 to 0.7 eV.

Considering that the irradiation process elevates the temperature to $T = 310$ K, the thermal flux J_{th} jumps from 107% to $\approx 180\% J_{exp}$, highly contradicting the experimental results.

Alternatively, the apparent thermal instability resulting from $E_m = 0.4$ eV can be lifted by a small increase in E_m , which significantly changes the situation. Figure 9(b) shows how the contribution of J_{th} evolves in comparison with J_{exp} as a function of the temperature ($290 \leq T \leq 400$ K), considering distinct

E_m values varying from 0.4 to 0.7 eV, but keeping D_0 constant ($D_0 = 5 \times 10^6 \text{ nm}^2 \text{ s}^{-1}$). It is clear that, for each E_m value, the increase of temperature causes the rise of J_{th} contribution to J_{exp} . On the other side, increasing E_m causes a reduction of J_{th} and enhances the film's thermal stability. Assuming $E_m = 0.5$ eV, $J_{th}(300 \text{ K}) \approx 0.023J_{exp}$ and $J_{th}(350 \text{ K}) \approx 0.32J_{exp}$. For $E_m \geq 0.6$ eV, the contribution of J_{th} can be neglected for irradiation temperatures $T \leq 400 \text{ K}$. Hence, J_{irr} must entirely produce the observed J_{exp} . According to Müller et al. [27], the thermal activation energies for the dewetting process do not depend on the Au film thickness h (for $15 \lesssim h \lesssim 35 \text{ nm}$) and correlates with $E_m > 1 \text{ eV}$. This result supports our suggestion that Au films' surface migration energy is somewhat larger than $E_m = 0.4 \text{ eV}$ estimated in Ref. [31]. In the following, we will examine the behavior of J_{irr} considering $E_m = 0.5 \text{ eV}$, which is a critical value delimiting a thermal controlled process ($E_m \lesssim 0.4 \text{ eV}$) and a purely electron-irradiation controlled process ($E_m \gtrsim 0.6 \text{ eV}$).

Figure 10(a) shows how the predicted $J_{tot} = J_{irr} + J_{th}$ behaves for each of the $E_d(r)$ models from Table 1. The curves are calculated for $p_e = 1/3$, $p_e = 1/4$, $T = 300 \text{ K}$, $E_m = 0.5 \text{ eV}$, and $D_0 = 5 \times 10^6 \text{ nm}^2 \text{ s}^{-1}$. The thermal contribution J_{th} is the same for all cases. For this choice of T and E_m , J_{th} is relatively small (see Fig. 10). All $E_d(r)$ models fit the J_{exp} data for an appropriated E_{d_0} value. This occurs because the $\Delta\Gamma$ term (Eqs. (3) and (4)) is more significantly affected by choice of p_e and p_f than by the film edge curvature effect on the elastic cross-section $\sigma(E_d(r))$. This observation denotes that the film thicknesses $h \geq 6.75 \text{ nm}$ do not cause significant changes in the surface binding energy $E_b(r)$ values (Table 2). It also points out that p_e and p_f are crucial parameters to be investigated. Using $p_e = 1/4$ in the calculations, we obtain $E_{d_0} \lesssim E_m$, which is not physically consistent, thus invalidating the $p_e = p_f$ hypothesis. Figure 10(b) shows how $J_{tot} = J_{irr} + J_{th}$ fit the J_{exp} points at different temperatures from 300 to 360 K. The increasing contribution of J_{th} implies the decrease of J_{irr} , obtained by enlarging E_{d_0} as the single fitting parameter. The results show that the irradiation process (J_{irr}) may occur concomitantly with the thermal contribution, playing a significant role for temperatures up to $T \approx 380 \text{ K}$. The TEM observations (Figs. 2 and 3) show that the Au film is polycrystalline. Nevertheless, grain boundary effects on the void's growth behavior are not particularly noticed. This observation is consistent with the hypothesis that void growth behavior is independent of the void sizes and shapes. From this point of view, our analysis reflects a general property of the Au film system. Figure 8 shows that the area retraction behavior $A(\Phi)$ scales

Fig. 10 . (a) $J_{tot} = J_{irr} + J_{th}$ curves ($T = 300$ K, $D_0 = 5 \times 10^6$ nm² s⁻¹, $E_m = 0.5$ eV, and $p_e = 1/3$) for the distinct $E_d(r)$ models presented in Table 1. J_{th} curve is the same for all cases and represents a fraction about 1% of J_{exp} ; (b) $J_{tot} = J_{irr} + J_{th}$ and J_{th} curves for distinct temperatures, calculated using the $E_d(r)$ model from Qu et al. [13], and the same D_0 , E_m and p_e parameters as in (a). The best fit approach renders E_{d_0} (300 K) = 1.65 eV, E_{d_0} (340 K) = 1.80 eV and E_{d_0} (360 K) = 2.13 eV.

with the total perimeter $P(\Phi)$ through a simple relation

$$A(P) = A_{mg} - 2.15 \times 10^{-3} P^2(\Phi). \quad (6)$$

This relation suggests that the film's void system can be represented by a number N of circular voids of equal or different sizes, or even by a single void with an area A and perimeter P satisfying Eq. (6) and the experimental data from Fig. 5. To demonstrate this hypothesis, we developed a finite difference approach (FDA) to calculate the $A(\Phi)$ evolution using the initial $A(\Phi = \Phi_i)$ value and the irradiation and

thermally induced atomic fluxes described in Eqs. (4) and (5). The area retraction behavior is calculated using small time increments $\Delta t = j^{-1} \Delta \Phi$. The FDA calculations are developed considering a system of $N = 37$ circular voids with the same radius $r = h$, consistent with Eq. (6) on this basis the FDA equations read

$$\begin{aligned}
 A_c(t + \Delta t) &= A_c(t) + \frac{dA_c}{dt} \Delta t, \\
 \frac{dA_c}{dt} &= -\frac{j}{\Omega} \frac{(J_{irr} + J_{th})P_c(t)}{h(t)}, \\
 P_c(t) &= 2\sqrt{N\pi(A_{mg} - A_c(t))}, \\
 h_c(t) &= \frac{V}{A_c(t)}.
 \end{aligned} \tag{7}$$

In these equations, A_c , P_c , and h_c are the calculated area, perimeter, and film height. J_{irr} is given by Eq. (4), J_{th} is given by Eq. (5), A_{mg} is the TEM micrograph area used to evaluate $A_c(t = t_i)$, and V is the total Au content volume within the micrograph obtained via RBS measurements. For a given temperature T and surface diffusivity D_s , the A_c values are adjusted to the measured ones shown in Fig. 5 by choosing an appropriate E_{d0} value. A least-square-fit approach determines the best choice of E_{d0} . Figure 11 shows how the calculated $A_c(\Phi)$ and $P_c(\Phi)$ values compare the corresponding experimental $A(\Phi)$ and $P(\Phi)$ ones. The calculation is done considering $E_d(r)$ behavior given by Yu et al. [22], $E_m = 0.5$ eV, $D_0 = 5 \times 10^6$ nm² s⁻¹, $p_e = 1/3$, $p_f = 1/4$, and $T = 300$ K rendering $E_{d0} = 1.43$ eV. At this point, it is worth noting that $E_{d0} = 1.43$ eV represents an upper limit value resulting from the use of upper limit values for the atomic jump probabilities p_e and p_f . The electron-atom collision causes the impinging atom's vibration, but the jump's success rate can be lower. A success rate of about 50% leads to jumping probabilities $p_e \approx 1/6$ and $p_f \approx 1/8$, rendering $E_{d0} = 0.95$ eV for the irradiation-induced flux process, which still is a consistent value within the boundary condition $E_d \geq E_m$. The same reasoning applies to the curve fitting approach used to calculate the results shown in Figs. 9 and 10. An important point to be noticed is that the analysis using the FDA method demonstrates that the results depend on the assumptions to estimate the irradiation and thermal effects and not on the calculation method or on the approximations to determine J_{exp} .

Fig. 11 . Finite Difference Approach (FDA) calculation fitting area A (a) and perimeters P (b). The calculations were done considering $T = 300$ K, $p_e = 1/3$, $p_f = 1/4$, $D_0 = 5 \times 10^6$ nm²· s⁻¹, and $E_m = 0.5$ eV.

5 Conclusions

In summary, the present study reports on the area retraction behavior presented by a discontinuous 6.75 nm thick Au film submitted to room temperature irradiations using 200 keV accelerated electrons. The area retraction behavior is phenomenologically modeled considering thermally and irradiation-induced atomic fluxes. The calculated atomic fluxes are compared with an estimated experimental flux derived from TEM observations of the film coverage area A and the total perimeter P of the void system. We demonstrate that A and P are two correlated quantities (Eq.(6)). This correlation supports the hypothesis that any perimeter segment represents the entire system, simplifying the atomic flux calculations.

The balance between thermally and irradiation-induced fluxes strongly depends on the choice of the surface diffusivity D_s parameters. The surface diffusivity parameters ($D_0 = 5 \times 10^6 \text{ nm}^2 \text{ s}^{-1}$ and $E_m = 0.4 \text{ eV}$) determined by Göbel and Blanckenhagen [31] within the temperature range from 330 to 773 K suggests that the systems thermal stability is very delicate. According to our calculations, for $E_m \lesssim 0.4 \text{ eV}$, thermally activated processes dominate the observed area retraction phenomenon even at room temperature. For $E_m \gtrsim 0.6 \text{ eV}$, the area retraction is entirely dominated by the irradiation process. For $E_m \approx 0.5 \text{ eV}$, our calculations show that thermally induced processes start to dominate at temperatures $T \gtrsim 380 \text{ K}$, which is consistent with previous studies in Au thin films (15 to 35 nm thick) [2, 30].

In general, our experimental results and their interpretation suggest that electron irradiation methods provide microstructure evolution behaviors at room or lower temperatures similar to the thermally activated processes developing at higher temperatures. In this sense, electron irradiation experiments become particularly interesting to explore surface located atoms' behavior and better understand their role in microstructural processes.

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Figures

Figure 1

(a) Schematic cross-section view of the samples. Notice the layer description, thickness information, and the electron irradiation direction indication; (b) Rutherford Backscattering measurement. The continuous lines denote a SIMNRA [24] simulation fit through the experimental points. The legends inform the detected atomic content.

Figure 2

(a) TEM micrographs showing the initial condition of the Au film (left) and the changes produced by an irradiation fluence $\Phi = 2.9 \times 10^{10} \text{ e}^- \text{ nm}^{-2}$ (right); (b) measured SAD ring patterns. The patterns are correlated with the left and right images in (a). Notice the fitted ring pattern using the Au crystallographic parameters.

Figure 3

TEM micrographs illustrating the films microstructure evolution as a function of the irradiated fluence Φ . Notice the fluence indication in the micrographs and the size indication in the upper left.

Figure 4

Illustration of the threshold contrast process to determine the void areas and perimeters. (a) original TEM micrograph, the white regions correspond to void images; (b) threshold contrast process to determine the voids areas; and (c) determination of the voids perimeters from the dark structures in (b).

Figure 5

(a) Film covered area A and (b) the integrated perimeter P of the void structures. A and P are expressed as a function of the irradiation fluence, Φ , and determined using the threshold contrast method illustrated in Fig. 4 (see text). The error bars correspond to the errors in the threshold contrast process. The continuous lines results from a least-square fit optimization using the functions presented in the figure.

Figure 6

Unscreened Rutherford elastic scattering cross-section, σ for 200 keV accelerated electrons impinging into an Au atom. σ is expressed as a function of the transferred energy E_d . The vertical dashed line corresponds to the maximum transferred energy.

e-beam direction

Figure 7

Schematic cross-section view of a film-void edge presenting an circular-like interface curvature and a segment of the film flat region. The curvature radius r corresponds to the film thickness h . Notice the representation of the possible jump directions at the films edge (p_e) and at the films flat regions (p_f).

Figure 8

Film coverage area A plotted as a function of the total voids perimeter P . The fitted line corresponds to a function $A(P) = A_{\text{mg}} - 2.15 \times 10^{-3} P^2$.

Figure 9

(a) Thermally-induced atomic flux, J_{th} (Eq. (5)) as a function of the irradiation fluence, Φ (continuous lines). The calculated curves are for $T = 300$ K and corresponds to the surface diffusivity parameters listed in Table 3. The square points represent the J_{exp} values (Eq. (2)), calculated using $pe = 1/3$ and $Ed(r)$ according to Ref. [22]. (b) J_{th}/J_{exp} ratio expressed as a function of the temperature T . The

calculations considers $D_0 = 5 \times 10^6 \text{ nm}^2 \cdot \text{s}^{-1}$ and distinct migration enthalpy E_m values from 0.4 to 0.7 eV.

Figure 10

(a) $J_{\text{tot}} = J_{\text{irr}} + J_{\text{th}}$ curves ($T = 300 \text{ K}$, $D_0 = 5 \times 10^6 \text{ nm}^2 \cdot \text{s}^{-1}$, $E_m = 0.5 \text{ eV}$, and $p_e = 1/3$) for the distinct $E_d(r)$ models presented in Table 1. J_{th} curve is the same for all cases and represents a fraction about 1% of J_{exp} ; (b) $J_{\text{tot}} = J_{\text{irr}} + J_{\text{th}}$ and J_{th} curves for distinct temperatures, calculated using the $E_d(r)$ model

from Qu et al. [13], and the same D0, Em and pe parameters as in (a). The best fit approach renders Ed0 (300 K) = 1.65 eV, Ed0 (340 K) = 1.80 eV and Ed0 (360 K) = 2.13 eV.

Figure 11

Finite Difference Approach (FDA) calculation fitting area A (a) and perimeters P (b). The calculations were done considering $T = 300$ K, $p_e = 1/3$, $p_f = 1/4$, $D_0 = 5 \times 10^6$ nm²· s⁻¹, and $E_m = 0.5$ eV.