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Bending of nanoporous thin films under ion radiation

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ABSTRACT

In general, fundamental understanding of radiation resistance of high surface density nanoporous materials and nanoporous coatings is severely lacking. In this contribution ion-induced bending phenomena are studied in free-standing nanoporous Au cantilevers with thickness in the range of 100 to 200 nm. Experiments were performed in a Tescan Lyra dual beam system with Ga⁺ ion irradiation normal to the sample surface up to a maximum fluence of $\sim 3 \times 10^{19} \text{ m}^{-2}$. Cantilevers bend towards the incident ion beam. It was found that the sensitivity of nanoporous Au samples to radiation-induced bending is substantially higher in comparison to the solid bulk counterparts. The process is described in terms of ion-induced coarsening of the structure top layers, which generates a volume contraction responsible for the bending moment. Therefore it is concluded that radiation-induced coarsening/sintering leads to negative swelling. Radiation-modified effective Young's modulus of the top layers was shown to influence essentially the fluence dependence of bending curvature. Model predictions agree well with our experimental findings showing that inhomogeneous radiation-induced coarsening of nanoporous structure results in bending and that nanoporous materials are less suitable for coatings in nuclear applications under the test conditions.

1. Introduction

Nanoporous metals attract considerable interest in science and engineering because of unique properties which originate from their 3D structure formed by a network of ligaments, nodes and open-cell porosity. Nanoporous gold (np-Au) is a typical example of nanoporous metals with unusually large specific surface area of interconnected ligaments of nanometer-scale characteristic dimensions. Controllable pore and ligament morphology of np-Au offers a suitable system for fundamental studies of a wide range of properties related to the structure of nanoporous materials.

In this paper we study the response of np-Au free-standing samples to irradiation with a Ga⁺ ion beam. The underpinning arguments for this study stem from: (i) the focused ion beam technique (FIB) is a natural tool to manipulate nano-sized objects; (ii) nanoporous metals may have a potential application as radiation resistant materials due to the high density of unsaturable sinks for radiation-induced interstitials and vacancies, which are represented by large amount of free surfaces [1,2]. In general, fundamental understanding of radiation resistance of high surface density nanoporous materials and nanoporous coatings is lacking. Investigations are devoted mainly to studies of radiation damage inside ligaments [2–8].

Here we would like to draw attention to radiation-induced coarsening of a nanoporous structure which may result in deterioration of initial properties of np-Au, such as volume fraction of metal, dimensional stability, mechanical properties etc. This effect has not received much attention in literature. Radiation-induced coarsening was mentioned in [1], where the response of nanoporous Au samples to irradiation with 400 keV Ne²⁺ ions to a fluence of $\sim 10^{19} \text{ m}^{-2}$ was studied. These irradiation parameters correspond to a uniform radiation damage of 1 dpa in the entire sample thickness of 150 nm. In our experiments the ion penetration range is much smaller than the sample thickness. We observed that ligaments as seen by scanning electron microscopy (SEM) are larger at the sample surface. We attribute this to ion-induced coarsening. Inhomogeneous coarsening results in a depth-dependent volume change which reveals itself by the bending of free-standing nanoporous cantilevers [9]. It will be shown that Ion Beam Induced Bending of nanoporous systems is a versatile tool, not only to (re)shape nanosized devices but also a measuring tool of physical properties of extremely fine nano-features of thin structures that are beyond the capacity of commonly employed contact-based techniques.

Below we describe the experimental procedure. Then we formulate a phenomenological model to account for the experimental observations. Finally, the model predictions are compared to the fluence

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dependence of cantilever curvature measured experimentally. The results obtained of nanoporous systems are discussed and confronted to the outcome of ion-beam aided manufacturing of dense solids.

2. Experimental

The precursor materials used for the present studies were commercial AuAg foils (Noris Blattgold GmbH, Schwabach, Germany) with thickness between 100 and 200 nm. Free-standing thin films of nanoporous gold were synthesized by free etching on 65% nitric acid solution. Foils with composition of $\text{Au}_{35}\text{Ag}_{65}$ and $\text{Au}_{25}\text{Ag}_{75}$ were dealloyed for times between 30 min and 1 day in order to achieve various ligament and pore sizes. The dealloyed samples were collected from the acid solution with gold transmission electron microscopy (TEM) grids and thoroughly rinsed with distilled water before drying in air. Thermal post-treatments for further coarsening were performed at up to 400 °C under Ar atmosphere. The TEM grids were finally mounted in an internally designed holder to position the films normal parallel to the ion beam in a dual beam FIB/scanning electron microscope (SEM) microscope (Lyra, Tescan, CZ).

The procedure to fabricate cantilevers from the free-standing film in the present work had to be adapted from that for the solid case [10] in order to minimize ion-induced changes in the nanoporous structure. Parallel lines approximately 3 μm long were cut with the FIB forming bridges that were posteriorly released in one end. The optimal width for the cantilevers to avoid rupture of the bridges and/or bending across the cantilevers width during the experiments was found to be of around 300 nm (Fig. 1). When the aforementioned parallel lines were cut below the optimal width the bridges collapsed by themselves in the middle, leaving equally sized edges in both sides similar to those seen in specimens subjected to tensile ductile fracture. Earlier experiments with larger cantilevers ($\sim 5 \times 3 \mu\text{m}^2$) showed irregular bending behavior due to cracks that appeared in eventual grain boundaries crossing the irradiated region.

A coarsened structure was observed under the scanned lines made amid the cantilevers cutting steps (Fig. 2) as well as in the irradiated cantilevers (Fig. 1). Interestingly, coarsening and grain-boundary cracks were also reported to result from ion irradiation at very low doses, i.e. a single imaging scan with the focused ion beam [11], and highly strained ligaments were observed across the FIB-induced cracks. A hint of ion-induced coarsening was also reported in [12], where a nanoporous gold pillar with diameter of 4 μm was produced by ion milling and analyzed with X-ray microdiffraction.

An intuitive picture of ion-induced coarsening can be provided based on the observations above, as follows. In the case of ion-irradiation, one may assume that a large amount of ligaments will rupture if their sizes are comparable to that of the displacement cascades. This collapse of ligaments is a pre-requisite for coarsening according to molecular dynamic (MD) simulations where the decrease of surface area was shown to lag behind the decrease in topological genus [13].

Fig. 1. Bending cantilevers with optimized dimensions.

Fig. 2. Coarsened ligaments in the ion-irradiated cutting tracks during the preparation of nanoporous cantilevers.

Additionally, ion-irradiation is expected to generate point defects that will diffuse and be absorbed preferentially at the surface steps, leading to either enhanced surface diffusion or direct surface smoothing via bulk transport [14]. In MD simulations of irradiation of gold ligaments with 1.5 keV primary knock-on atoms, coarsening appeared to be dose-rate independent, suggesting that the effect is due to individual cascade effects [1]. Ion-induced coarsening can be compared to thermal coarsening; assuming (i) direct breakage of small ligaments by cascades instead of spontaneous collapse by Rayleigh instabilities [13] and (ii) surface smoothing due to the radiation-induced generation of point defects instead of thermal activation. Based on this reasoning, we propose a model that assumes a coarsening gradient as the main factor generating the bending moment in irradiated nanoporous cantilevers.

It should be noted that Ga may form complex phases with bulk Au. We have searched in TEM diffraction analysis, in conjunction with energy dispersive spectroscopy as well as with X-ray diffraction for Au–Ga phases but no Au–Ga complexes could be detected. Next, it is known that stacking faults and stacking fault tetrahedral loops may be formed due to point defect condensation in bulk Au after ion radiation. This is as expected since a faulted or unfaulted dislocation loop becomes always favorable above a certain critical radius of a disc of vacancies (or interstitials), i.e. a critical radius of 2–4 nm in metallic systems (depending on the surface free energy). Also a dislocation loop is always energetically more favorable than a spherical point defect cluster for large enough values of number of point defects. It can be shown that theoretically unfaulting of unstable stacking fault loops are expected when the radius of the loop becomes larger than 10 nm in Au. Since the thickness of the ligament lies in the same order of magnitude unfaulted loops are not likely of these sizes but rather faulted loops of very small sizes. Defect loops could be observed in TEM mode but due to the small size stacking fault contrast was not seen in TEM mode. Stacking faults were not observed inside the ligaments, also possibly due to reorientation of stacking faults in a dipolar orientation by free surface (image force) effects and annihilations. So, the general conclusion which will hold for dense solids is: upon ion radiation at moderate energies, say below 1 MeV, point defects clusters are produced. For metals, spherical clusters will collapse to either faulted or unfaulted dislocations loops depending on the size and specific stacking fault energy. Spherical voids and disks are not stable at room temperature irradiation according to predictions based on linear elastic continuum mechanics.

3. Model of ion-induced bending of nanoporous metal

In our previous papers we have studied the bending behavior of solid cantilevers made from Au [15] and Al [10]. It was found that the bending under ion beam irradiation cannot be explained just by the generation of isolated point defects and implantation of Ga^+ ions since their effects are too small. Instead, our experimental findings can be explained by a mass transfer from the irradiated layer to the deeper

layers beyond the Ga^+ penetration range due to gliding/diffusion of interstitial clusters. Mobile clusters collide with each other and form sessile clusters. The amount of material transferred to the unirradiated zone grows with the fluence and leads to local volume increase resulting in bending. Ion-induced bending of nanoporous cantilevers cannot be explained by this mechanism. The obvious reason is that interstitial clusters cannot escape the ligament in which they were produced. In the present experiments, samples had ligament sizes of the same scale or smaller than the implantation range of 30 keV Ga^+ ions as simulated with SRIM [16] for normal incidence. The implantation range for these parameters is about 30 nm while the characteristic length/diameter of ligaments in nanoporous gold prepared by free dealloying lies usually between 5 and 35 nm [17].

Stopping range of ions in matter (SRIM, version 2012.03) simulations allow us to see the effects of ions impinging upon a solid target. A typical result for SRIM of a gold surface exposed to a 30-kV Ga ion beam is shown in ref. [9, 16]. As an ion generates an approximately fixed number of defects, the shape of the ion penetration distribution is then the same as the shape of the distribution of defects created through ionic knock-on effects. The region beneath the surface facing the ion beam holds the vast majority of defects, leading to an anisotropic defect concentration across the specimen. This has the potential to lead to the formation of a bending moment. The defect distribution induced through ion collisions can be modeled as symmetric and triangular which was done for a dense solid case (see ref. [9]). As the stress profile scales linearly with the defect profile, the aggregate compressive force is then represented by the area of the stress profile. For porous systems the physical reasons for bending might be more complex than for the dense solid case as will be explained in the following. In the present experiments of porous systems, samples have ligament sizes of the same scale or smaller than the implantation range of 30 keV Ga^+ ions as simulated with SRIM [16] for normal incidence. The implantation range for these parameters is about 30 nm while the characteristic length/diameter of ligaments in nanoporous gold prepared by free dealloying lies usually between 5 and 35 nm [17].

The nanoporous specimens differed from the bulk counterparts in that the sensitivity to irradiation was considerably higher, and also the displacement induced by the cutting step, i.e. the position of the cantilevers in the beginning of the experiments deviate slightly from the plane of the supporting film. These observations support the argument that the governing mechanism in these samples is different from the solid cases.

To construct a model of nanoporous sample bending under ion irradiation we explore a new hypothesis based on coarsening of the nanoporous structure. The assumption of the model is that ion-induced coarsening (or sintering) of the nanoporous structure is accompanied with compaction which results in contraction of the subsurface ligament structure subjected to irradiation. The nanoporous cantilever is freestanding in the sense it is without constraints against mechanical deformations; therefore the inhomogeneous volume change causes the cantilever to bend towards the ion beam. It seems that the ion-induced coarsening is similar to the effects of annealing on nanoporous gold structures which leads to coarsening of pores and ligaments [18–22]. The underlying mechanism of thermal coarsening and ligament growth is related to surface diffusion [13,22–24].

The driving force for coarsening is the reduction of total surface area of ligaments. Evidently, ion beam irradiation effectively enhances atomic mobility in a similar way as the temperature increase. Several mechanisms control ion-induced coarsening/sintering:

- migration of radiation-induced interstitial atoms to the ligament surface and surface diffusion of adatoms as controlled by the ligament surface curvature
- migration of small point defect cluster inside ligaments and to ligament surfaces which provide a ‘plastic’ deformation mechanism.

As was discussed in [10,15] high mobility of point defect clusters, both vacancy and interstitial types, has been confirmed experimentally (for recent results see [7,8]) and by means of MD simulations [25–27]. In addition, purely ballistic effects play an important role. Ligament sizes are distributed in a size range. If the ligaments are too small, i.e. comparable with the size of displacement cascades produced by primary knock-on atoms, a cascade would cause ligaments to break or collapse.

Other effects may arise from high local curvature of small ligaments – enhanced sputtering, for instance. Irradiation of gold nanoparticles and thin films with 25 keV Ga^+ ions have been simulated with Molecular Dynamics and the sputtering yield was found to be size-dependent with a maximum of roughly three times that of a bulk surface [28]. This effect can be expected to result in high amounts of internal redeposition and subsequent reconfiguration or densification of irradiated nanoporous structures.

In the following our goal is to estimate the relative volume change of the cantilever material as a function of ligament mean size, ion fluence and depth from the sample surface. Consider time evolution of a small volume element $V(y, t)$ inside the ion-irradiated cantilever, here y is the distance from the cantilever surface (Fig. 3).

The volume of all ligaments V_{Au} in the volume $V(y, t)$ does not change during irradiation, while volume of pores V_p decreases with time due to coarsening and shrinkage of empty space. The relative volume change due to coarsening is given by

$$\Omega(y, t) = \frac{\Delta V_p(y, t)}{V_{Au0} + V_{p0}} \quad (1)$$

where $\Delta V_p(y, t) = V_p(y, t) - V_{p0} \leq 0$ is the volume decrease from the initial state. The volume fractions of gold and the porosity are

$$f_{Au}(y, t) = f_{Au0} \frac{1}{1 + \Omega} \quad (2)$$

$$f_p(y, t) = \frac{f_{p0} + \Omega}{1 + \Omega} \quad (3)$$

where f_{Au0} and f_{p0} are the initial volume fractions.

It is likely that the coarsening is isotropic in all directions, therefore the relative change in linear dimensions – the linear contraction – is estimated as

$$\lambda(y, t) = (1 + \Omega(y, t))^{1/3} - 1 \quad (4)$$

As in our previous papers [10,15] we use the analogy with the thermoelasticity. Unlike the solid cantilever the properties of the irradiated nanoporous cantilever such as the contraction and (effective) Young's modulus E depend on position; hence we use formulas of Ref.

Fig. 3. Schematic view of coarsening and contraction of cantilever irradiated with ions.

[29] describing the thermal stress in an inhomogeneous beam, in which the linear expansion and Young's modulus are functions of position y as shown in Fig. 3. In equations of thermoelastic bending of the cantilever beam [29] we replace the linear thermal expansion $\alpha T(y)$ with the linear contraction $\lambda(y, t)$ and obtain the curvature radius in our problem

$$\frac{1}{R} = \frac{M_T I_{E0} - P_T I_{E1}}{I_{E0} I_{E2} - I_{E1}^2} \quad (5)$$

where

$$I_{En}(t) = \int_0^{d(t)} E(y, t) y^n dy, \quad n = 0, 1, 2 \quad (6)$$

$$P_T(t) = \int_0^{d(t)} E(y, t) \lambda(y, t) dy \quad (7)$$

$$M_T(t) = \int_0^{d(t)} E(y, t) \lambda(y, t) y dy \quad (8)$$

Integration is carried out over the cantilever thickness $d(t)$ which decreases with time due to ligament sputtering by incident ions and compaction due to coarsening.

$$d(t) = d_0 - Y \omega j t + \int_0^{d'} \lambda(y, t) dy \quad (9)$$

where Y is the sputtering yield, j is the ion flux and ω is the atomic volume; the upper integration limit d' is selected beyond the ion penetration range in the undamaged region where $\lambda = 0$.

The deflection z of the cantilever towards the ion beam is related to the curvature by [30]

$$z = x^2/2R \quad (10)$$

where x is measured from the fixed end of the cantilever (Fig. 1).

Note that in Eqs. (6)–(9) the modulus $E(y, t)$ is the effective Young's modulus of the volume element $V(y, t)$, which should not be confused with Young's modulus of an individual ligament. In our model we use the linear theory of elasticity. At high ion fluences, when the cantilever deflections are large, one may expect plastic deformation of ligaments and even microcracking on the far side of the cantilever.

3.1. Kinetics of coarsening

To find the linear contraction $\lambda(y, t)$ we construct below a simple model with unknown parameters which we will determine from comparison with experimental data. The total surface area of ligaments S , the characteristic mean ligament size L and the characteristic mean spacing between ligament (pore size) L_p is a minimal set of variables describing the structure of the volume element under consideration (Fig. 3). Parameters defined above are related to gold, pore and total volumes

$$V_{Au} = ASL \quad (11)$$

$$V_p = BSL_p \quad (12)$$

$$AS_0 L_0 + BS_0 L_{p0} = V_0 \quad (13)$$

where A and B are factors associated with the topology of a particular nanoporous structure. In the following we assume that A and B do not change essentially with time.

It is natural to assume that (i) the structure with small ligaments coarsens faster and (ii) the coarsening rate is proportional to the defect production rate $K(y) = j \omega K_{SRIM}(y)$ measured in units 'displacements per atom per second' ($K_{SRIM}(y)$ is the distribution of Frenkel pairs over the sample depth per incident Ga^+ ion). Hence, the mean ligament size changes with time according to

$$\frac{dL}{dt} = \frac{\xi_{Au}}{L^{n-1}} K(y), \quad n > 1 \quad (14)$$

where n depends on dominating mass transport mechanism, $\xi_{Au} > 0$ is a constant. The solution to this equation can be represented in the form

$$L^n = L_0^n + \beta_{Au} n \omega^{\frac{n+3}{3}} K_{SRIM}(y) \varphi \quad (15)$$

where φ is the ion fluence, β_{Au} is the dimensionless constant.

In a similar way we construct the equation for the pore size L_p

$$\frac{dL_p}{dt} = -\frac{\xi_p}{L_p^{m-1}} K(y) \quad (16)$$

where $\xi_p > 0$ is a constant, the minus sign corresponds to decrease of mean spacing between ligament. The solution to Eq. (16) is given by

$$L_p^m = L_{p0}^m - \beta_p m \omega^{\frac{m+3}{3}} K_{SRIM}(y) \varphi \quad (17)$$

where β_p is the dimensionless constant.

In the volume element under consideration the volume of solid gold does not change with time, i.e. $SL = \text{const}$, therefore the fluence dependence of the total area is given by

$$S = \frac{S_0 L_0}{L} = S_0 L_0 \left(L_0^n + \beta_{Au} n \omega^{\frac{n+3}{3}} K_{SRIM}(y) \varphi \right)^{-1/n} \quad (18)$$

Using Eqs. (11), (17) and (18) we find the pore volume

$$V_p(y, \varphi) = V_{p0} \frac{L_0}{L_p} \frac{L_p(y, \varphi)}{L(y, \varphi)} \quad (19)$$

and the fluence dependence of the relative volume change

$$\Omega(y, \varphi) = (1 - f_{Au0}) \left[\frac{L_0}{L_{p0}} \frac{L_p(y, \varphi)}{L(y, \varphi)} - 1 \right] \quad (20)$$

Using Eq. (13) we can obtain the relation between the initial size of pores L_{p0} and other parameters of the nanoporous structure

$$L_{p0} = g L_0 \frac{1 - f_{Au0}}{f_{Au0}} \quad (21)$$

where $g = A/B$.

3.2. Effective Young's modulus of nanoporous Au

The curvature radius given by Eq. (5) depends on Young's modulus $E(y, t)$. Note that the curvature radius does not change if we substitute $E(y, t)/E_{nAu}$ for $E(y, t)$, where E_{nAu} is Young's modulus of the undamaged nanoporous material. This is an important property of the bending phenomenon: it is the relative modulus ('relative stiffness') $E(y, t)/E_{nAu}$ that contributes to bending rather than the absolute value of Young's modulus. Schematically the relative modulus is the ratio

$$\frac{E(y, t)}{E_{nAu}} \propto \frac{E_{\text{upper layer}}}{E_{\text{bottom layer}}} \quad (22)$$

which controls the amount of bending caused by coarsening. A higher modulus of the upper layer facilitates bending and vice versa: if the upper layer is more compliant than the bulk the bending is less pronounced.

The Gibson-Ashby scaling relation [31,32] is used frequently to describe the dependence of Young's modulus on density of porous materials, which in our problems reads

$$\frac{E(y, \varphi)}{E_{nAu}} = \left(\frac{f_{Au}}{f_{Au0}} \right)^k = (1 + \Omega(y, \varphi))^{-k} \quad (23)$$

where $k \sim 2$ for the classical Gibson-Ashby relation.

Being designed for low-density cellular (foam) materials, the Gibson-Ashby relation does not automatically apply to nanoporous

gold. The network topology of a nanoporous structure differs from the cellular architecture of foams. However, in some materials, this relation is working quite well.

Liu and Jin [33] report that in a Pt-doped nanoporous gold, in which the network connectivity was maintained constant, Young's modulus varied with relative density according to a power-law relation with an exponent $k = 2.2 \pm 0.1$, which agree well with the classical Gibson-Ashby law ($k = 2$).

It has also been observed that the elastic modulus of nanoporous gold decreased by more than one order of magnitude in structure coarsening [33,34] during which the relative density changed only little.

Mathur and Erlebacher [35] examined Young's modulus of free-standing, large-grained and stress-free nanoporous gold films of 100 nm thick over a controlled range of ligament sizes. Measurements by a buckling-based method [36] have shown a dramatic increase in the effective Young's modulus with decreasing ligament size, especially below 10 nm.

All these results indicate that the mechanical response (including the elastic modulus) of nanoporous metals depends not only on the relative density but also on the topology of the nanoporous structure. The network connectivity [33,34,37] has been suggested as a structural feature that accounts for the anomalous behavior of Young's modulus of nanoporous gold. Indeed, strength and stiffness would decrease if a good number of ligaments in nanoporous metal are 'broken' and the network structure is less connected compared with a foam materials with the same density. In other words, the effective density of the material with only load-bearing ligaments is smaller than the total density.

The hypothesis seems to be promising, but then questions arise as to how the network connectivity parameter can be defined and experimentally measured in the nanoporous metals, and how it can be correlated to mechanical properties. Mameka et al. [37] proposed a connectivity parameter, which is a ratio between the diameter of the unit cell of nanoporous structure and the diameter of the closed rings in a network of load-bearing paths.

Fig. 4 shows the influence of coarsening during thermal annealing on the elastic modulus of the as-dealloyed nanoporous samples [33]. It was found that Young's modulus of high density nanoporous samples changed little when the structure size was coarsened from 5 nm up to 300 nm during annealing. On the contrary the elastic modulus of low density samples decreased dramatically after coarsening. Note a non-monotonic behavior of Young's modulus at volume fraction of gold less than 0.35.

Fig. 4. Variations of Young's modulus during coarsening of nanoporous samples with various initial relative densities, which may increase during coarsening particularly for low-density samples (after Ref. [33]).

In literature the coarsening of nanoporous structure was proposed to proceed by the 'pinch-off' of some ligaments due to Rayleigh instability [13,38,39] and simultaneous removal (healing) of dangling ligaments by surface diffusion [13,40]. Evidently, low density samples with thin ligaments are more prone to 'pinch-off' damage caused by annealing which result in decrease of network connectivity. Increasing ligament size and relative density would decrease the aspect ratio of ligaments, which decreases the probability of 'pinch-off' and prevents the network connectivity reduction as was observed in [33].

We believe that the influence of ion-induced coarsening on properties of nanoporous metals is similar to that of thermal coarsening discussed above. Moreover, the ion irradiation with its sputtering effects is especially efficient to destroy thin ligaments thereby reducing the connectivity and effective Young's modulus. As the sample become denser with larger ligaments the radiation-induced coarsening results in Young's modulus increase. In our model the relative modulus is a function of ligament and pore sizes and initial volume fraction of gold

$$\frac{E(y, \varphi)}{E_{Au}} = \left(\frac{f_{Au}}{f_{Au0}} \right)^k = \left(f_{Au0} + (1 - f_{Au0}) \frac{L_0}{L_p} \frac{L_p(y, \varphi)}{L(y, \varphi)} \right)^{-k} \quad (24)$$

To model the non-monotonic dependence on ligament size we will adjust the power law exponent k for 'small' and 'large' ligament sizes.

4. Comparison with experiments

Fig. 5 shows the fluence dependence of curvature for nanoporous samples of different thicknesses and ligament sizes, which are denoted as 'Thickness/Ligament'. One set of samples was irradiated with 20 keV Ga^+ ions; all other samples were irradiated with 30 keV Ga^+ ions. The samples had their structure tailored by means of varying dealloying times and one was coarsened thermally. In fact, the sample that was thermally coarsened to the point where the ligament sizes reached the same scale of the film thickness presented the same bending rate as annealed solid Au samples.

Fig. 5 exemplifies the increased bending sensitivity to ion fluence of nanoporous samples when compared to bulk samples (labelled as 89/89). The increased sensitivity of the nanoporous samples is evidenced by the fact that the thickness of the solid cantilever used for comparison was nearly half of the nanoporous ones.

The four other samples deserve a closer look. The argument of ion-induced ligament collapse and coarsening would predict higher bending rate per fluence for finer nanoporous structures. However, the finer of the structures produced in this study, which was dealloyed for 30 min ($L \sim 25$ nm), presented a lower bending dependence on fluence

Fig. 5. Fluence dependence of curvature for np-samples with different thicknesses and characteristic lengths. Eq. (10) was used to determine the curvature.

Fig. 6. The distribution of Frenkel pairs over the sample depth per incident Ga^+ ion at normal incidence. The ‘monolayer collisions, surface sputtering’ option of SRIM [16] was selected with displacement energy 44 eV [41].

than the sample dealloyed for 3 h ($L \sim 45$ nm). The reason for such a behavior is the anomalous dependence of Young’s modulus on ligament size during coarsening of small-sized nanostructures (see below).

Depending on size distribution of ligaments an incident ion can travel through a ‘surface’ ligament and hit a ligament in deeper location. On average in nanoporous materials the ion penetration range is larger than in solids. To take this into account in our model, which is a mean-field approximation, the defect generation rate $K_{\text{SRIM}}(y)$ is

calculated for an amorphous target of 50% density of solid gold (Fig. 6). In reality, nanoporous gold density depends on fluence and depth y , however for our qualitative model such a refinement is a second order correction.

The initial fraction of gold in all calculations is 0.3. The initial ligament size L_0 was measured in a sample micrograph using the rotationally averaged FFT power spectrum. To stay in the framework of our model the initial value of L_{p0} was evaluated using Eq. (21) with $g = 0.45$. Other parameters of the model were adjusted to reproduce the experimental dependence of curvature radius on fluence: $\beta_{\text{Au}} = 10^4$, $\beta_p = -3.0 \times 10^{-2}$, $n = 2$, $m = -0.5$.

First we show the dependence of np-Au geometrical parameters on fluence of 30 keV Ga^+ ions. Fig. 7 demonstrates that in the near surface region the volume fraction of gold increases drastically after irradiation to a fluence of $2 \times 10^{19} \text{ m}^{-2}$ which is a typical maximum fluence in these bending experiments.

Fig. 8a shows depth dependence of ligament size and pore sizes after radiation-induced coarsening (initial parameters and fluences correspond with Fig. 7). The fluence dependence of the ligament size at a distance of 5 nm from the surface is presented in Fig. 8b. This distance can be considered as a maximum depth which can be seen by SEM in real samples.

Fig. 9 shows the values of the FFT characteristic sizes for samples with initial average ligament sizes of ~ 27 and ~ 42 nm. The FFT characteristic size is defined as the position of the first maximum in the dependence of FFT intensity versus wave vector. For comparison the model predictions for the sum of ligament and pore sizes are plotted. Examples of the nanoporous structure at different fluence values are

Fig. 7. Depth dependence of gold volume fraction (a) and porosity (b) at two values of ion fluences. The initial ligament and pore sizes $L_0 = 46$ nm and $L_{p0} = 42$ nm.

Fig. 8. (a) Depth dependence of ligament size and pore sizes at fluences $2 \times 10^{18} \text{ m}^{-2}$ (dashed curves) and $2 \times 10^{19} \text{ m}^{-2}$ (solid curves). (b) Fluence dependence of the ligament size at a depth of 5 nm. Solid and dashed curves corresponds to ligament and pore sizes respectively.

Fig. 9. Evolution of characteristic FFT size with ion irradiation for two distinct initial average ligament sizes (symbols). Solid curves represent the sum of ligament and pore sizes calculated with the model.

shown in Fig. 10. Densification can be clearly seen at the last irradiation step for the sample with smaller ligament size (Fig. 10c).

In our experiment it was observed that the bending rate of nanoporous structures with ligament sizes of ~ 20 nm was lower than the bending rate of nanoporous structures with 46 nm ligaments. Such a behavior cannot be explained with the power law exponent $k > 0$ in the Gibson-Ashby relation, Eq. (24). We managed to describe bending of nanoporous structures with small ligaments using the power law exponent $k = -2$. Fig. 11 shows depth dependence of Young's modulus (Eq. (24)) at a fluence of 10^{19} m^{-2} for two types of scaling relation: for the initial ligament size 20 nm the exponent $k = -2$ in Eq. (24), for the initial ligament size 46 nm the exponent $k = 2$. In case of small ligament sizes we multiplied the right-hand-side of Eq. (24) by a factor of 10 in order to emphasize that undamaged nanoporous material has a higher Young's modulus than the irradiated subsurface material (as we mentioned above multiplication of the modulus by a constant does not change the curvature).

Fig. 12 shows the behavior of Young's modulus at a depth of 20 nm. As in Fig. 11, the exponents $k = -2$ and $k = 2$ were used in Eq. (24) for the initial ligament sizes of 20 nm and 46 nm, respectively. Fig. 12b

Fig. 11. Depth dependence of Young modulus at a fluence of 10^{19} m^{-2} for two types of scaling relation (24).

was plotted as a parametric dependence $K(20 \text{ nm}, \varphi)$ versus $L(20 \text{ nm}, \varphi)$, where the parameter is the fluence φ that changes from 0 to $3 \times 10^{19} \text{ m}^{-2}$. Note the similarity of model calculations (Fig. 12b) with Fig. 4 which shows a compilation of experimental data on the effect of annealing on effective Young's modulus.

In Figs. 13–15 we compare the curvature radius as predicted by the model with the curvature found from processing of the experimental data. Fig. 13 shows that a good agreement with experimental data can be obtained if we use different values for the power law exponent k for 'small' and 'large' ligament sizes.

Fig. 14 compares the predicted fluence dependence of the cantilever curvature with experimental data at initial thicknesses 144 and 196 nm. In both cases the initial ligament size is the same $L_0 = 46$ nm, and the classical Gibson-Ashby relation ($k = 2$) was used in calculations.

Fig. 15 shows the fluence dependence of cantilever curvature at Ga^+ ion energies 20 and 30 keV. The model curves reproduce the experimental trend. As it could be expected the ion beam with lower energy produces lower bending rates, because of smaller ion penetration range and lower efficiency to create radiation defects and the consequent structure coarsening.

Fig. 10. Evolution of nanoporous structure under irradiation for samples with $L_0 \sim 27$ nm (a–c) and 42 nm (d–f) showing unirradiated, intermediate ($\sim 7.5 \times 10^{18} \text{ m}^{-2}$) and final states. Maximum fluences corresponds to Fig. 9. In all SEM micrographs the field of view is $1 \times 1 \mu\text{m}^2$.

Fig. 12. Young modulus as a function of fluence (a) and ligament size (b) at a depth of 20 nm.

Fig. 13. Fluence dependence of cantilever curvature: influence of initial ligament size and scaling relation type. Symbols denote experimental data for the initial ligament size 21 nm (squares) and 46 nm (circles). The dashed curve was calculated with the classical Gibson-Ashby relation ($k = 2$) for the initial ligament size 46 nm. The solid curve was calculated with $k = -2$ in Eq. (24) for the initial ligament size 21 nm. The dashed-dotted curve corresponds to calculations for the initial size 21 nm with the classical Gibson-Ashby relation ($k = 2$). Ga^+ ion energy is 30 keV.

As an additional test of the model we calculated the thickness decrease of irradiated nanoporous samples. The total thickness decrease exhibits a weak dependence on ligament size. At the ligament size 46 nm and the fluence $1.5 \times 10^{19} \text{ m}^{-2}$ the thickness decrease due to sputtering and coarsening is estimated as

$$\Delta d_{\text{sputtering}} = -Y\omega\varphi \approx -4 \text{ nm} \quad (25)$$

$$\Delta d_{\text{coarsening}} = \int_0^{d'} \lambda(y, t) dy \approx -7 \text{ nm} \quad (26)$$

where $Y = 15.5$ is the gold sputtering rate. The sum of these values well agree with measurements. However, it should be noted that experimental measurement of thickness decrease is difficult, because it is comparable with the ligament size and surface irregularities.

5. Conclusions

The stability of nanoporous gold cantilevers with respect to ion beam irradiation was studied. All samples bent toward the 30 kV Ga^+ beam. It was observed that the sensitivity of nanoporous samples to irradiation is considerably higher as compared to solid samples. A novel

Fig. 14. Influence of initial thickness on the fluence dependence of curvature. Symbols denote experimental data for the sample thickness 144 nm (squares) and 200 nm (circles). The model curves are calculated with $k = 2$ in Eq. (24). The initial ligament size is 46 nm. Ga^+ ion energy is 30 keV.

Fig. 15. Influence of Ga^+ ion energy on the fluence dependence of curvature. Symbols denote experimental data for the ion energy 20 keV (squares) and 30 keV (circles). The model curves are calculated with $k = 2$ in Eq. (24). The initial ligament size is 46 nm.

message of the model proposed here is that the bending of nanoporous gold samples under ion irradiation can be explained by coarsening and sintering of the ligament structure which results in decrease of porosity and shrinkage of the sample subsurface layer.

It seems that nanoporous materials with open-cell porosity are ill-suited for nuclear applications as structural materials and differ

considerably in the phenomenon of swelling near surfaces in homogeneous dense materials. On the one hand, a high specific surface area of nanoporous gold facilitates the removal of radiation defects from the bulk of ligaments; on the other hand, it stimulates the radiation-induced coarsening and sintering, which results in negative swelling, i.e. dimensional instability and the usual positive swelling is compensated by the ongoing sintering effects.

An analogy with thermoelasticity was used to convert the inhomogeneous volume change due to radiation-induced coarsening into bending curvature of a free-standing cantilever. The curvature radius depends essentially on the effective Young's modulus of the damaged nanoporous structure. It turned out that in order to explain experimental behavior of the cantilever under irradiation we had to assume non-monotonic dependence of effective Young's modulus on mean ligament size: decreasing for small ligament sizes and increasing, of the Gibson-Ashby type, for larger ligament sizes.

The model calculations reproduces experimental observations on ion-beam-induced bending of nanoporous Au samples. It goes without saying that basically the choice of Ga irradiation onto metallic porous media was directed by the FIB system but we believe the work has generic meaning, when taking into account the mass ratios, energies stopping powers (electronic and nuclear) of the corresponding ions and substrate atoms. Regarding the size limitations for structures fabricated by this method, one must consider an interplay between all parameters that define the depth of the ion-induced volume changes, i.e. film thickness, ion source and energy and defect kinetics. Controlled bending in both directions (towards and opposed to the ion beam) has been demonstrated elsewhere by us [9,15] varying beam energy and cantilever thickness and no influence was observed of the cantilever's length (in the range of 1 to 2 μm) or width (in the range from 1 μm up to 20 mm) [9,15,42].

Throughout this study, irradiation was performed by scanning the whole area. This was done in order to obtain uniform curvatures along the cantilever length for each fluence, allowing for the use of the thermoelasticity analogy. This does not need to be the case, however, as sharp folding of thin films achieved by irradiation of lines have been reported before for dense solids [43,44].

To conclude, Ion Beam Induced Bending of nanoporous systems is not only a promising tool in the fabrication of micro- and nanosized devices or MEMS components but also a method of characterization of the structure-property relationship of extremely fine nano-features of thin structures that are beyond the capacity of typical physical contact-based techniques.

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Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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