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Full Length Article

On the mechanism of ion-induced bending of nanostructures

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ABSTRACT

This contribution concentrates on ion-induced bending phenomena which may serve as a versatile tool to manufacture nanostructured devices. In particular bending was studied in free standing Au cantilevers. The preparation and irradiation of the cantilevers were performed using a TESCAN LYRA dual beam system. Cantilevers with thicknesses ranging between 90 and 200 nm were irradiated with 30 keV Ga ions normal to the sample surface up to a maximum fluence of $\sim 3 \times 10^{20}$ Ga/m². The bending of the cantilevers towards the incident beam is discussed in terms of local volume change due to accumulation of radiation-induced vacancies and substitutional Ga atoms in the Ga implantation layer, as well as due to accumulation of interstitial type clusters in the region beyond the Ga penetration range. A model is proposed to explain the observations, based on a set of rate equations for concentrations of point defects, i.e. vacancies, self-interstitials and implanted Ga atoms. The influence of preexisting defects is also discussed. The work shows that an in-depth understanding the ion-beam bending can play a predictive role in a quantitative control in for the micro- and nanofabrication of small-sized products.

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1. Introduction

Focused ion beam (FIB) technology came a long way from its advent in the seventies, when their utility for maskless doping of silicon was first proposed. As the feasibility of different liquid metal sources was proved and the beam spot sizes were reduced to the range of tenths of nanometers, ion beam technology became an advantageous method for sub-micron fabrication and maskless processes such as imaging, implantation, etching and deposition [1]. Today it plays an important role in applications which range from micro- and nanofabrication to sample preparation and materials characterization. Assessment of the properties of submicron- and nanometer-sized samples is challenging, however, because of the difficulties in fabricating specimens which are ideally free of preparation artifacts. FIB milling techniques for nanosample preparation and characterization can result in undesirable effects such as bending and microstructural modification due to ion implantation. In particular, dual beam systems combining focused ion beam and scanning electron microscope (FIB-SEM) are frequently used for sample preparation and characterization. Typically, the FIB gun operates with 30 keV Ga⁺ ions and is used for cutting away or building up structures on a material surface with a resolution of about 50 nm.

A rather recent development has been the ability to bend small-nanosized structures by ion irradiation in a reproducible manner, with a good potential for the manufacturing of 3D nanodevices in photonics and metamaterials. It has been demonstrated e.g. by the fabrication of free-standing plasmonic nanogratings structures with the FIB [2]. Ion induced bending (IIB) was observed in multi-wall carbon nanotubes [3], thin film cantilevers of silicon nitride [4], amorphous-metal bilayers [5], a series of metals and nitrides irradiated with different ion species [6], as well as nanoporous metallic pillars [7], proving the versatility of the technique.

The phenomenon was first reported by Yoshida et al. [8] who were able to bend a W₂S thin film cantilever towards or away from the incident Ga⁺ ion beam by changing its energy. Borschel et al. [9] observed the opposite relation between ion energy and bending direction using GaAs nanowires. In both cases, the bending momentum was argued to be related to the ion implanted range in relation to the sample thickness – due to relaxation of internal stresses in the former and generation of crystallographic defects in the latter. A study on ZnO nanowires reported no recovery of bending after annealing up to 800 °C, suggesting that bending has been made permanent by the nucleation and motion of dislocations [10]. Attempts to explain ion beam bending mechanism were based on the stress generated by ion implantation and gas/vacancy complexes, thermal gradients induced by ion irradiation or the movement of knock-on atoms along the film thickness [4–6]. The observation of 'no bending' in the case of electron beam

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irradiation shows that the thermal expansion due to irradiation-induced heating is not significant in the case of metallic nano-objects [5]. Ion-induced amorphization has also been suggested as a main factor in ion-induced bending of semiconductors [11]. Romano et al. [12] investigated ion bending of Ge nanowires and suggested a mechanism of ion-induced amorphization and subsequent densification. Pecora et al. [13] observed recovery of bending in Si nanowires after annealing and attributed bending to the generation of a crystalline/amorphous interface. Ishii et al. [14] confirmed that most of the stress lies in the amorphous phase for the case of Si and developed a model of relaxation of ion-induced defects to account for the flux dependence of stress evolution. In metals, the bending process can be thought to result from volumetric expansion caused by ion implantation. From an atomistic point of view, stresses generated in the free standing sample of thin film are generally attributed to the accumulation of defects during ion irradiation. The Bragg Coherent X-ray Diffraction Imaging (BCDI) has been recently used to resolve lattice distortion in gold nanoparticles with high precision [17]. The results suggest that the use of FIB causes large lattice distortions, which are consistent with a damage microstructure dominated by vacancies. At larger ion fluences, typical for FIB milling, formation of a dislocation network was reported. However, in general the underlying physics of the bending effect is not clear. Understanding of this phenomenon is crucial for attaining high accuracy and predictability, which will enable the use of IIB as a reliable method for manipulating the shape and geometry of functional nanostructures in nanodevices.

In this paper we present detailed investigations of IIB on metallic cantilevers taking Au as a typical example of an fcc structured material. The next section presents experimental details on sample preparation and characterization. Section 3 reports experimental results. In Section 4 we discuss possible bending mechanisms and present a new kinetic model based on a set of rate equation for concentrations of implanted Ga atoms and point defects (PD). The influences of preexisting dislocations and PD clusters created in displacement cascades are also discussed.

Modeling results discussed in Section 5 show that the bending under ion beam irradiation cannot be explained just by the generation of isolated PDs and deposition of Ga ions since their effects are too small. We argue that IIB can be explained by a mass transfer from irradiated cantilever layer to the deeper layers due to gliding/diffusion of interstitial clusters which are formed in displacement cascades. Mobile clusters collide with each other and form sessile clusters and interstitial dislocation loops. The amount of material transferred to the unirradiated zone grows with the fluence and leads to local volume increase resulting in bending.

2. Experiments

Thin gold films were deposited by evaporation (Temescal FC-2000 electron-beam evaporator) on mechanically polished sodium chloride substrates. These were posteriorly dissolved in water, allowing the films to float and to be collected with a TEM grid so that the films were free-standing. The grids containing the films were annealed at 340 °C for 30 min in argon atmosphere to minimize the influence of defects, such as grain boundaries and dislocations which could have been introduced during the films deposition and manipulation. They were then placed in an in-house developed holder that is able to position the samples surface perpendicular to the ion beam in a Tescan Lyra dual-beam FIB instrument.

To prepare the cantilevers and to perform the bending experiments (Fig. 1) the film specimens were irradiated with 30 keV Ga⁺ ions at normal incidence.

Fig. 1. Ion-beam irradiation of the cantilever (a); the implantation profile of Ga⁺ ions is shown schematically. Deflection of Au cantilever ($d_0 = 144$ nm) after irradiation to a fluence of $1.4 \times 10^{20} \text{ m}^{-2}$ (b).

The bending cantilevers were fabricated with FIB as illustrated in Fig. 2. The procedure was chosen to avoid bending during the cutting steps and to provide a clear view to the cantilever during the experiments. Two areas were cut on both sides of the interest region and bent up by irradiating the lines that connect them to the rest of the film. Finally the remaining “bridge” was cut forming the cantilever which will be irradiated. A current of 200 pA was used for cutting and 40 pA for all other steps. Care was taken to reduce as much as possible the ion exposure of the regions of interest prior to the bending experiments.

The irradiation was performed over an area slightly larger than the cantilevers to assure that all parts of it were equally processed. A parallel scanning strategy was used, meaning that each scanning pixel in the selected area would be irradiated sequentially for a dwell time of 1 μs . A minimum of 300 scans (equivalent to a fluence of $\sim 3.0 \times 10^{19} \text{ Ga/m}^2$ at 40 pA) was used for each measurement step, before the cantilever would be imaged by scanning electron microscopy. The irradiation/imaging steps continued until bending reached an advanced stage. The cantilever deflection was measured from the SE images using ImageJ [15] and Engauge [16], considering the perspective correction required by the 55° tilt of the electron beam in relation to the ion beam.

The Ga concentration in the irradiated films was measured by energy-dispersive X-ray spectroscopy (EDS) in an FEI-Philips FEG XL30S operating at an acceleration voltage of 5 kV. A sample with initial thickness of 144 nm was used and irradiation with progressive fluences was performed without additional preparation over areas of $8 \times 8 \mu\text{m}$. Element quantification was obtained using the semi-quantitative, standardless eZAF method; comparative analysis is nevertheless possible as all measurements were made using identical parameters in a single sample.

3. Experimental results

Fig. 3 presents the deflection and curvature plots for several irradiation fluences. Intermediate lines regarding smaller steps were omitted for clarity. The curvature along the cantilevers

Fig. 2. Sequence of steps for preparing the bending cantilevers (a–c). Ion irradiation is performed over an area slightly larger than the cantilever (d).

remains mostly uniform after irradiation to small fluences, with higher deviations close to the cantilever tips and far ends. The increase in curvature during the first few steps is quite small, pointing out the feasibility of inducing the deflection of such structures in a precise manner. As irradiation proceeds, however, the curvature assume a U-shape, as can be clearly seen in Fig. 3d for the film with initial thickness of 89 nm. This observation can be understood considering that the angle between the ion beam and the cantilever normal changes as bending proceeds. As that angle increases, so does the sputtering yield, while the ion implantation depth decreases. This results in heterogeneous thickness and implantation depth along the cantilever length resulting in a non-uniform curvature.

The averaged curvature $1/R$ measured in the middle region of the cantilevers is plotted against fluence in Fig. 4. Thinner films are more sensitive to irradiation and all curves show a gradual increase of slope. This was hypothesized to be related to the thickness reduction due to sputtering. The concentration of Ga for different fluences as measured by EDS is shown in Fig. 5. The values refer to the average concentration along the film thickness. The measurements dispersion is attributed to the low concentrations of gallium, close to the precision, but the trend agrees with the model prediction.

4. Model of PD kinetics

For a better understanding of the deformation of the films we present here a dedicated model of radiation-induced bending due to point defect accumulation in a crystalline thin film. It is obvious that we need a gradient in the defect generation as a function of depth to explain any bending and curvature. As an energetic ion travels through a solid material, its momentum and energy are transferred to the latter by interactions with its atomic nuclei and electrons. When a recoil atom acquires enough kinetic energy to be displaced, it gives rise to PD such as pairs of vacancies and self-interstitial atoms (SIA) and small clusters of PD [18,19]. In metals, most of the primary defects are created in collision cascades initiated by recoil atoms knocked on from regular lattice positions. Point defects interact with each other during the cascade development. After a fast relaxation stage of the cascade the remaining PD defects continue to migrate by thermal diffusion, resulting e.g. (i) in the recombination of vacancies with self-interstitials or implanted ions and (ii) the diffusion of PD to sinks such as surfaces, pre-existing dislocations, grain-boundaries and PD clusters [19]. When a surface atom has enough energy to surmount the surface binding energy, it will be sputtered away from the bulk. Monte Carlo simulations can be

Fig. 3. Deflection and curvature evolution of Au cantilevers with nominal initial thickness of 200 nm (a, b) and 89 nm (c–f) irradiated with 30 keV Ga with parallel (a–d) and serial (e–f) scan strategies. The labels next to the lines indicate the fluence in units of Ga ions/m². The curvature 1/R was calculated from experimental data using Eq. (14). The error bars of the experimental data are not repeated in the calculated curvature representation.

performed using SRIM code [20] to estimate the ion implantation rate, defect generation rate and sputtering yield. Alternatively, a more sophisticated Monte Carlo code TRiDYN based on the sputtering version of the TRIM program for multicomponent targets can be used [21,22]. TRiDYN computes range profiles of implanted ions, composition profiles of the target and sputtering rates for a dynamically varying target composition. It is known that SRIM code overestimates the number of stable PD as compared to more realistic MD simulations [23]. The reason is that SRIM does not consider the defect recombination during collisional stage of displacement cascade relaxation. However in the following we will use SRIM simulations without corrections as an upper estimate of PD production rate, since one of the objectives of this work is to estimate the maximum possible effect of PD on bending.

In the model description we consider a cantilever beam in the form of a metal film of thickness d_0 irradiated with Ga ions. The ion beam irradiation creates displacement cascades in the subsurface region of the film. PDs produced in displacement cascades are distributed within the penetration depth of ions. The time-dependent rate equations for concentrations of vacancies C_v , self-interstitial atoms C_i , interstitial Ga atoms C_{iGa} and substitutional Ga atoms C_{Ga} are as follows

$$\frac{dC_v}{dt} = K(y)(1 - C_v) - \alpha D_i C_i C_v - \alpha D_{iGa} C_{iGa} C_v - Z_v \rho D_v C_v + D_v \Delta C_v, \quad (1)$$

$$\frac{dC_i}{dt} = K(y)(1 - C_v - C_{Ga}) - \alpha D_i C_i C_v - Z_i \rho D_i C_i + D_i \Delta C_i, \quad (2)$$

Fig. 4. Fluence dependence of the curvature $1/R$: comparison of experimental data with model calculations. The initial thickness of cantilevers is indicated near the corresponding curves. Dash-dotted curves are given by the sum of contributions to bending from vacancies and substitutional atoms, Eq. (10), and sessile clusters, Eq. (20), with the parameters $\varepsilon = 1.4 \times 10^{-2}$, $n_d = 440$ and $h = 20$ nm (see explanation in Section 5). The dashed curve is calculated only with contributions of vacancies and substitutional atoms to volume change, Eq. (10), (initial thickness 200 nm).

Fig. 5. Concentration of Ga in the gold film with initial thickness of 144 nm as measured by EDS (circles) and predicted by the model (see explanation in Section 5).

$$\frac{dC_{iGa}}{dt} = K_{Ga}(y) + K(y)C_{Ga} - \alpha D_{iGa}C_{iGa}C_v - Z_i \rho D_{iGa}C_{iGa} + D_{iGa}\Delta C_{iGa}, \quad (3)$$

$$\frac{dC_{Ga}}{dt} = \alpha D_{iGa}C_{iGa}C_v + Z_i \rho D_{iGa}C_{iGa} - K(y)C_{Ga}, \quad (4)$$

where concentrations are defined per lattice site, $K(y)$ is the generation rate of PD (we assume that the rate for vacancies is the same as for self-interstitials) as a function of distance from the film surface, $K_{Ga}(y)$ is the implantation rate of Ga, $\alpha = 4\pi R_{iv}/\omega$ is the recombination rate constant, $R_{iv} \sim a$ is the radius of spontaneous recombination (a is the lattice spacing), ω is the volume per lattice site, $D_{i,v,iGa}$ are the diffusion coefficients ($D_{i,iGa} \gg D_v$), ρ is the dislocation density and $Z_{i,v}$ are dislocation capture efficiencies for vacancies and interstitial atoms [19]. Capture efficiencies depends on dislocation configurations. For an edge dislocation $Z_{i,v}$ are estimated as [19]

$$Z_{i,v} = 2\pi \left(\ln \frac{L}{r_{i,v}} \right)^{-1}, \quad (5)$$

where $r_{i,v}$ are capture radius of PD by a dislocation and L is the mean spacing between sinks. Dislocations attract interstitial atoms more strongly than vacancies, therefore $r_i > r_v$ and $Z_i > Z_v$.

The PD generation rate and Ga implantation rate are calculated with SRIM

$$K(y) = j\omega K_{SRIM}(y), \quad (6)$$

$$K_{Ga}(y) = j\omega K_{SRIM}^{Ga}(y), \quad (7)$$

where j is the flux of Ga^+ ions at the film surface, $K_{SRIM}(y)$ is the distribution of Frenkel pairs over the film depth per incident Ga^+ ion and $K_{SRIM}^{Ga}(y)$ is the probability density to find the incident ion at a depth y when it spends the kinetic energy to collisions with the lattice atoms.

Although the most energetically favorable site for Ga is a substitutional lattice site in Au, also the kinetics of interstitial Ga atoms is considered in Eq. (3), which are generated by the knock-on process during the subsequent radiation process from the substitutional Ga atoms.

The physical meaning of different terms in the set of equations can be explained conveniently by using Eq. (1) as an example: $\alpha D_i C_i C_v$ mutual recombination of vacancies and self-interstitial atoms controlled by thermally-activated diffusion of SIA since in metals $D_i \gg D_v$; $\alpha D_{iGa} C_{iGa} C_v$ recombination of implanted thermalized Ga with vacancies; $Z_v \rho D_v C_v$ absorption of vacancies by dislocations; $D_v \Delta C_v$ diffusion of vacancies from the implanted layer to external surfaces.

For simplicity, diffusion coefficient of self-interstitial atoms and interstitial Ga ions are assumed to be the same.

PDs can be absorbed also by grain boundaries. However, it is assumed here that the sink strength of grain boundaries is low as compared to dislocations and external surfaces. This means that the distance between grain boundaries is larger than the dislocation spacing and the film thickness.

The model equations takes into account the diffusion-limited reactions between vacancies, interstitial atoms and dislocations, which are controlled by the mean temperature of the cantilever. The ion irradiation can cause the temperature increase in the cantilever. In order to estimate an upper bound of temperature increase δT over the temperature of sample holder we assume that: (i) in the irradiated part of the cantilever of length l the kinetic energy of ions completely transforms into heat (no energy loss to sputtering, defect creation, etc.); (ii) the cantilever side-walls are thermally insulated (no heat dissipation by radiation to a surrounding medium) and (iii) the heat flows through the unirradiated cantilever neck of the length l_0 into the holder that is kept at constant temperature (see Fig. 2). The timescale of heat transfer across the cantilever is very small. For a 200 nm film it is estimated as $d^2/\kappa \sim 3 \times 10^{-10}$ s, where $\kappa = 1.27 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ is the thermal diffusivity of gold. Therefore, on a larger timescale the production rate of heat per unit time per unit volume can be considered to be uniform across the thickness of the irradiated part of the cantilever $Q = jE_{Ga}/d$, where E_{Ga} is the Ga^+ energy. The temperature distribution along the cantilever can be found from the steady state one-dimensional equation of heat conduction with the heat source Q . The maximum temperature increase is observed at the cantilever tip

$$\delta T = \frac{jE_{Ga}l^2}{2dk} \left(1 + \frac{2l_0}{l} \right), \quad (8)$$

where k is the thermal conductivity.

For the flux used in our study $j = 3 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$ and parameters $E_{Ga} = 30 \text{ keV}$, $l = 5 \text{ } \mu\text{m}$ and the thermal conductivity of gold $k = 314 \text{ W m}^{-1} \text{ K}^{-1}$, even for a very thin cantilever of thickness $d = 50 \text{ nm}$, the temperature increase is small $\delta T = 0.34 \text{ K}$. Therefore in the following the cantilever temperature is assumed to be close to room temperature.

The impingement of the film with energetic ions results in film sputtering, i.e. movement or receding of the film boundary with the rate

$$v = \frac{dy}{dt} = j\omega Y \quad (9)$$

where Y is the sputtering yield (number of sputtered atoms per incident ion). For Eqs. (1)–(3) we use zero boundary conditions at both external surfaces.

The implanted ions and PD distributions result in an inhomogeneous volume change. The bending is a consequence of the stress originating from the volume change localized within the layer where implanted ion and PD are distributed. The relative volume change $\Omega = \Delta V/V$ associated with PD is given by the sum

$$\Omega_{PD} = C_v(y) \frac{\Delta\omega_v}{\omega} + C_{Ga}(y) \frac{\Delta\omega_{Ga}}{\omega} \quad (10)$$

where $\Delta\omega_v$ is the vacancy relaxation volume and $\Delta\omega_{Ga}$ is the excess volume associated with substitutional Ga atom. Here we neglected the contribution of interstitial atoms because under typical conditions the remaining concentrations of interstitial atoms are very small due to high diffusion mobility at room temperature. The relaxation volume of vacancies is negative in all metals. The excess volume associated with substitutional Ga atom depends on the specific film material, being negative in Au (Table 1). It can be deduced from the dependence of lattice parameter on Ga concentration in solid solutions.

Another contribution to the volume change originates from absorption of PD by dislocations bounding prismatic loops (both preexisting and radiation-induced), which may result in dislocation climb. The rate of local volume change due to dislocation is given by

$$\frac{d}{dt} \Omega_{dist} = \rho(Z_i D_i C_i + Z_i D_{iGa} C_{iGa} - Z_v D_v C_v) \quad (11)$$

The volume change due to dislocations is always positive even when both interstitials and vacancies are mobile, because of dislocation bias to absorption of interstitial atoms ($Z_i > Z_v$) [19]. To evaluate the bending due to the inhomogeneous volume change

$$\Omega = \Omega_{PD} + \Omega_{dist} \quad (12)$$

We use an analogy with the thermoelasticity. It is well known that thermoelastic stresses due to the linear thermal expansion $\alpha T(y)$ results in bending of beams and multilayered materials

[28]. In the equations of thermoelastic bending of the cantilever beam we replace the linear thermal expansion $\alpha T(y)$ with the linear expansion/contraction.

$$\lambda(y) = \Omega(y)/3 \quad (13)$$

and find the solution to the problem of cantilever bending induced by ion irradiation. The strain in the film is given by

$$\varepsilon_{xx} = \varepsilon_0 + \frac{1}{R} \left(y - \frac{d}{2} \right), \quad \varepsilon_0 = \frac{1}{d} \int_0^d \lambda(y) dy, \quad \frac{1}{R} = \frac{12}{d^3} \int_0^d \lambda(y) \left(y - \frac{d}{2} \right) dy \quad (14)$$

where $d = d_0 - vt$ is the cantilever thickness, x is the coordinate in the direction of the free end, R is the radius of curvature at the neutral plane and ε_0 is the axial strain in the x -direction at the neutral plane. The stress in the cantilever is given by

$$\sigma_{xx}/E = \varepsilon_0 + \frac{1}{R} \left(y - \frac{d}{2} \right) - \lambda(y) \quad (15)$$

where E is the Young's modulus. The deflection of the beam (Fig. 1) is related to curvature by

$$v = x^2/2R \quad (16)$$

The bending direction depends on the sign of the total volume change and the location of the layer with respect to the neutral axis in which the radiation defects are created.

The assumption so far is that the model considers only PD contribution to the evolution of the film microstructure. Mobile interstitial atoms can form clusters which can evolve into dislocation loops. MD simulations carried out to date predict that a fraction of point defect created in cascades is produced in interstitial clusters which are stable and highly mobile at room temperature [29]. These clusters can accumulate in the undamaged region of the film. It should be noted that the radius of curvature Eq. (14) depends only on the inhomogeneous volume change. There is no dependence on elastic moduli. One may expect that the volume change can generate high stresses leading to plastic deformation.

5. Modeling results and discussion

To make a connection between experiments and theoretical description the set of equations formulated above was solved numerically by the method of lines using the RADAU code [30]. Material parameters used in simulations are listed in Table 1. The initial thickness of the film was 200 nm. The dislocation density was assumed to be low $\rho < 1/d_0^2$.

According to SRIM simulations, during irradiation of Au film with 30 keV Ga⁺ ions PDs are generated mostly within a range of about 30 nm (Fig. 6). The “monolayer collisions – surface sputtering” option of SRIM was selected with displacement energy 44 eV [31].

Concentration profiles of vacancies, substitutional Ga atoms and interstitial atoms are shown in Fig. 7. It is seen that the concentration profiles moves inside the film as the material is removed from the surface due to sputtering. The concentration of vacancies is very high, whereas concentrations of interstitial atoms are very low due to fast diffusion to external surfaces. It should be noted that distributions of vacancies and Ga atoms in the subsurface region of the film do not depend on time after a short transient period. Vacancies are essentially immobile, since at the room temperature the timescale of vacancy diffusion across the projectile range is $(30 \text{ nm})^2/D_v \cdot 10^5 \text{ s}$.

The concentration of Ga at the surface reaches values of about 5 at.%. By running the SRIM simulation with the composite target

Table 1
Material parameters used in model calculations.

Parameter	Value	Ref.
Flux of Ga ⁺ ions j , m ⁻² s ⁻¹	3×10^{19}	
Temperature, T , K	300	
Atomic volume, ω , m ⁻³	1.7×10^{-29}	
Sputtering yield, Y (SRIM)	15.5	
Recombination rate constant, α , m ⁻²	3×10^{20}	
Diffusion coefficient of vacancies, D_v , m ² s ⁻¹	$2.43 \times 10^{-6} \exp(-0.89 \text{ eV}/k_B T)$	[24]
Diffusion coefficient of interstitials, D_i , m ² s ⁻¹	$5 \times 10^{-6} \exp(-0.06 \text{ eV}/k_B T)$	[25]
Relaxation volume of vacancies, $\Delta\omega_v$	-0.37ω	[26]
Relaxation volume of interstitial atoms, $\Delta\omega_i$	$\approx \omega$	
Misfit volume of gallium, $\Delta\omega_{Ga}$	-0.076ω	[27]
Dislocation density, ρ , m ⁻²	10^{11}	
Dislocation capture efficiency for SIA, Z_i	3.3	
Dislocation capture efficiency for vacancies, Z_v	3

Fig. 6. The production rate of PD $K(y)$ and the implantation rate of Ga $K_{Ga}(y)$ were calculated with SRIM for 30 keV Ga ion implanted into amorphous Au target at normal incidence.

$Au_{95}Ga_5$ we found that influence of implanted Ga on the PD production rate and the sputtering yield is in the range of a few percent. For this reason we believe that SRIM is an adequate tool for our problem; usage of dynamic TRiDYN code [21] for calculations of the PD production rate and the sputtering yield would not change our results essentially. Moreover the average Ga concentration derived from the model well agree with experimental measurements (see below).

The local volume change due to vacancies and Ga atoms is negative (Fig. 8) and results in bending towards the ion beam. Both vacancies and substitutional Ga atoms contributes to volume

change. However the contribution of substitutional Ga atoms is small because of their small misfit volume.

Fig. 4 compares the cantilever curvature measured in the experiment with the model prediction. The dashed curve is the fluence dependence of the curvature caused by isolated vacancies and substitutional Ga atoms. Fig. 4 shows that the generation of isolated PD cannot explain quantitatively the bending effect ion beam irradiation. A homogeneous distribution of preexisting dislocations would make the model prediction even worse since these dislocations introduce positive volume change in the subsurface region, which would result in a bending away from the beam. In the model described above there is no accumulation of radiation damage, except the subsurface layer. After a short transient period the steady state profiles of PD and implanted Ga ions are formed. For this reason the cantilever curvature depends only on maximum vacancy concentration, the thickness of damaged layer and the current cantilever thickness. Assuming triangular profile of vacancy concentration, it can be easily shown by direct integration of Eq. (14) that

$$\frac{1}{R} = \frac{1}{3} C_{vmax} \left| \frac{\Delta\omega_v}{\omega} \right| h \frac{3d(t) - 2h}{d(t)^3}, \quad (17)$$

where C_{vmax} is the maximum vacancy concentration, h is the thickness of damaged layer and $d(t) = d_0 - vt$ is the cantilever thickness. We have checked that at $C_{vmax} = 0.05$ and $h = 20$ nm Eq. (17) well reproduce the time dependence of curvature derived from the numerical solution. Eq. (17) contains no dependence of curvature on initial thickness of the cantilever, i.e. the model predicts that upon reaching the same thickness cantilevers of different initial thicknesses would exhibit the same curvature. However our experiments show that the curvature does depend on initial thickness.

Fig. 7. Concentration profiles of PD and implanted Ga atoms. Irradiation time is indicated near curves. The left boundary of the film is moving to the right (indicated with arrow) because of sputtering. One second of irradiation time corresponds to a fluence of $3 \times 10^{19} \text{ m}^{-2}$.

Fig. 8. Depth dependence of volume change due to vacancies and substitutional Ga atoms after irradiation for 10 s (ion fluence $3 \times 10^{20} \text{ m}^{-2}$).

A possible reason of high value of bending observed experimentally is the following. Redistribution of material between top and bottom layers due to migration of SIAs and the interstitial clusters formed in cascades can be responsible for cantilever bending. Incoming Ga ions and primary knock-on atoms create cascades of atomic displacements which relax into a distribution of defects. Not all defects appear as single interstitial atoms or isolated vacancies. Molecular dynamic simulations of cascades indicate that a significant fraction of the interstitial population is produced in 'sessile' and 'glissile' clusters [19,32]. The grouping of SIAs into clusters is significant because these defects are thermally stable and they can migrate away from their parent cascades. In the undamaged region (without cascades) the mobile clusters can form sessile clusters due to collisions with each other and absorption of single SIAs. Eventually these clusters may grow into dislocation loops. Contribution of one atom in the sessile clusters to the volume increase of the film is about the relaxation volume of SIA, i.e. $\Delta\omega_i\omega$. Assuming that sessile clusters form homogeneously across the undamaged region, the volume increase during time interval dt can be estimated as

$$d\Omega_{cl} = \Delta\omega_i \frac{\varepsilon j n_d}{d_0 - h - vt} dt \quad (18)$$

where n_d is the total number of defects generated by a Ga ion, $\varepsilon \ll 1$ is the fraction of interstitial atoms in mobile clusters which go to formation of sessile clusters. Assuming that ε weakly depends on the cantilever thickness, we find the relative volume increase due to mass transfer from the irradiated zone

$$\Omega_{cl} = \frac{\Delta\omega_i}{\omega} \frac{\varepsilon n_d}{Y} \ln \frac{d_0 - h}{d_0 - h - vt}. \quad (19)$$

The curvature is given by

$$\begin{aligned} \frac{1}{R} &= \Omega_{cl} \frac{4}{(d_0 - vt)^3} \int_h^{d_0 - vt} \left(y - \frac{d_0 - vt}{2} \right) dy \\ &= 2\varepsilon \frac{\Delta\omega_i}{\omega} \frac{n_d}{Y} \frac{h(d_0 - h - vt)}{(d_0 - vt)^3} \ln \frac{d_0 - h}{d_0 - h - vt}, \end{aligned} \quad (20)$$

Note that the lower integration range is limited to the thickness of damaged layer. There is no accumulation of excess volume in this layers because cascades create new clusters and destroy existing ones due to cascade overlap and the effect of radiation-induced mixing [19,33,34].

In Fig. 4 dash-dotted curves are given by the sum of contributions to bending from vacancies and substitutional atoms, Eq. (10), and sessile clusters, Eq. (20). The number of defect n_d was estimated with SRIM; the thickness of damaged layer $h = 20 \text{ nm}$

was taken from calculations of PD kinetics (Fig. 7); the parameter $\varepsilon = 1.4 \times 10^{-2}$ was adjusted to reproduce the behavior of all three experimental curves. The dashed curve in Fig. 4 was calculated only with contributions of vacancies and substitutional atoms Ω_{PD} ; it demonstrates that bending caused by isolated PD is small as compared to bending due to sessile clusters. We conclude from Fig. 4 that Eq. (20) well agrees with the experimental dependence of curvature on fluence and initial cantilever thickness. Fig. 9 shows the fluence dependence of the relative volume increase in the unirradiated region of the cantilever due to formation of sessile clusters. The volume increase or swelling Ω_{cl} is very high and reaches values of several tens of percent (compare with Fig. 8).

Here, it is also relevant to mention that the cluster hypothesis of bending is supported by our previous observation that bending was not removed by annealing at 200°C for 5 h, whereas bending due to isolated PD would anneal completely. No recovery of bending was also observed in ZnO nanowires annealed at temperatures up to 800°C [10].

It is reasonable to assume that the mobile interstitial clusters formed during cascade evolution are composed from Au and Ga interstitial atoms in the same proportion as the concentration of Au and Ga in the irradiated zone. This means that mobile clusters deliver Ga atoms to the unirradiated zone. Consider the cantilever at a steady state after a transient period of ion beam irradiation. Assuming a triangular profile of substitutional Ga atoms in the irradiated zone, from the balance of Ga fluxes

$$j = YjC_{Ga}^{(s)} + \varepsilon j n_d C_{Ga}^{(s)} / 2 \quad (21)$$

We can estimate the surface concentration of Ga $C_{Ga}^{(s)}$

$$C_{Ga}^{(s)} = \left(Y + \frac{\varepsilon n_d}{2} \right)^{-1} \quad (22)$$

Due to the flux of Ga atoms $\varepsilon j n_d C_{Ga}^{(s)} / 2$ concentration of Ga in the unirradiated zone C_{Ga} increases with time similar to volume increase given by Eq. (18) and (19)

$$C_{Ga} = \frac{\varepsilon n_d}{Y} \frac{C_{Ga}^{(s)}}{2} \ln \frac{d_0 - h}{d_0 - h - vt} \quad (23)$$

The average Ga concentration is a sum of two contributions from irradiated and unirradiated zones

$$\bar{C}_{Ga} = \frac{h C_{Ga}^{(s)}}{2(d_0 - vt)} \left[1 + \frac{\varepsilon n_d}{Y} \frac{(d_0 - h - vt)}{h} \ln \frac{d_0 - h}{d_0 - h - vt} \right] \quad (24)$$

Fig. 9. Fluence dependence of the relative volume increase (swelling) in the unirradiated region of the cantilever due to formation of sessile clusters. Initial thicknesses of cantilevers are indicated in the figure.

Fig. 5 shows the Ga concentration evaluated by averaging the numerical solution to Eqs. (1)–(4) (dashed curve denoted as ‘PD model’) and the Ga concentration given by Eq. (24) (dash-dotted curve denoted as ‘PD model + clusters’).

6. Conclusions

The study demonstrates the ability to bend small structures with sub-micron precision in a controlled manner using the focused ion beam. A quantitative relationship between curvature and fluence has been derived which proved to be helpful in controlling micro- and nanofabrication of small-sized products. Details of our findings include:

- (1) A series of bending experiments with cantilevers made from Au was performed and it was observed that the cantilevers of various thickness always bended towards the incident beam.
- (2) The experimental data are discussed in terms of local volume change due to accumulation of vacancies and substitutional Ga atoms. To this end the model for PD kinetics in the crystalline thin films under irradiation with energetic ions has been formulated. Accumulation of vacancies and implanted ions in the subsurface region of the film leads to local volume change. Using the analogy with the thermoelectricity, the strain, stresses and the bending deflection of a free standing cantilever irradiated with ions were found.
- (3) It was found that the bending under ion beam irradiation cannot be explained just by the generation of isolated PDs and deposition of Ga ions since their effects are too small. Instead, our experimental findings can be explained by a mass transfer from irradiated cantilever layer to the deeper layers 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.
- (4) Our findings show that application of FIB to prepare samples causes accumulation of radiation defects and may lead to contamination of the whole sample thickness with Ga.

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