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Highly pressurized Kr agglomerates in sputtered Si films

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Abstract

High resolution electron microscopy experiments are presented for a plasma-sputter-deposited Si film with a high Kr concentration. The amorphous layer deposited shows an oscillating Kr concentration. The Kr resides in very small agglomerates of size <1 nm. Bending measurements show that the pressure in the Kr agglomerates is very high, 3.9 GPa. Hardness measurements show that this pressure is limited by the fracture stress of the deposited film.

1. Introduction

In previous publications [1–3] we reported a study on the incorporation of Kr in thin Kr–Si films, produced by Kr plasma sputter deposition. These layers were characterized by a variety of techniques, including positron beam analysis, Raman spectroscopy, energy-dispersive X-ray spectroscopy (in cross-secton and in plane geometry), cross-sectional scanning electron microscopy and Mössbauer spectroscopy. The results clearly indicate that ion-assisted growth leads to a strong reduction in open volume, and that the Kr resides in very small clusters. This article adds new information on the Kr–Si films obtained by high resolution electron microscopy (HREM) and by measurements of the planar stress and the microhardness of the films.

2. Experimental details

Thin Kr–Si films were produced by sputtering of Si in a low pressure Kr plasma, in a similar way to that described in ref. 4. Kr–Si films with an area of 14 nm diameter were deposited on a Si ⟨100⟩ wafer 250 μm thick and of 20 mm diameter at a temperature of 583 K and a substrate bias of -50 V, using a Si target at a potential of -1.5 kV. The Si flux J_{Si} at the substrate was roughly constant at 4×10^{15} cm^{-2} s^{-1}, while the Kr flux J_{Kr} at the substrate could be varied between 4×10^{14} and 4×10^{16} cm^{-2} s^{-1} by varying the duty cycle (DC) of the pulsation of the substrate potential between 1 and 100% at 0.5 Hz. For the experiments described here, two samples were made. For the bending experiments a layer of 21.2 μm was deposited with $J_{Si} = 5.9 \times 10^{15}$ cm^{-2} s^{-1}, $J_{Kr} = 2.5 \times 10^{16}$ cm^{-2} s^{-1} and a DC of 50%, resulting in a local Kr concentration $C_{Kr} = 5.0$ at.%, whereas for the HREM experiments a layer of 4.9 μm was deposited with $J_{Si} = 3.4 \times 1010^{15}$ cm^{-2} s^{-1}, $J_{Kr} = 1.3 \times 10^{16}$ cm^{-2} s^{-1} and a DC of 30%, resulting in $C_{Kr} = 4.8$ at.%. The later sample was prepared for cross-sectional HREM by cleaving the wafer into 2 mm × 1 mm × 0.5 mm chips. These chips were glued together with the thin layers facing each other. Next, the sample was mechanically polished to a thickness of 10 μm and ion beam thinned to electron transparency. HREM observations were done using a JEOL 4000 Ex/II electron microscope operated at 400 kV. The study was focused on the incorporation of Kr in the amorphous Si layer and not on the defects formed in the Si substrate.

3. Results and discussion

Figure 1 shows a high resolution electron micrograph of the substrate in the ⟨110⟩ orientation together with the thin film. The film–substrate interface is sharp; there is no sign of polycrystalline growth in the region close to the substrate, contrary to what was suggested in refs. 2 and 3. Instead of clusters or bubbles of Kr atoms, a regular sequence of dark and bright bands is observed in the amorphous layer. These bands are interpreted as sublayers with alternating high and low average electron scattering power. If an image is made with a small objective aperture, regions in which elec-

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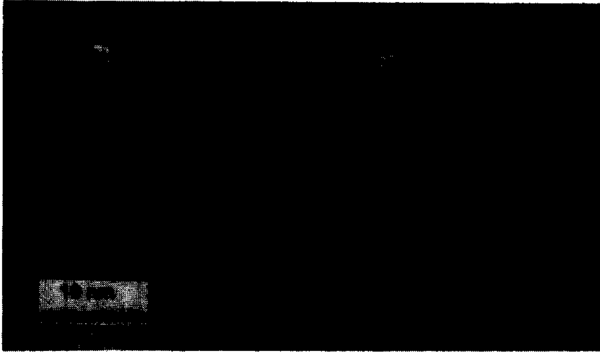

Fig. 1. High resolution image of the Si substrate (left) in the ⟨110⟩ orientation, together with the amorphous layer of Si and Kr (right). In the amorphous layer, one can see sublayers (arrowed) with alternating dark and bright contrast, having a period of 1.3(1) nm.

trons are scattered as larger angles show up darker than the surrounding parts. It is indeed observed that the difference in contrast between the dark and bright bands decreases with increasing objective aperture. Since Kr has a higher electron scattering factor than Si, the dark and bright bands may be interpreted as layers with alternating high and low Kr concentrations. The period of these sublayers is measured as 1.3(1) nm. The formation of sublayers can be understood as resulting from the processing of the material; Si is continuously sputtered at a rate of 0.65(10) nm s^{-1}, while Kr is injected with a DC of 30% at 0.5 Hz. This indeed leads to a period of about 1.3 nm. Inert-gas desorption experiments on Ar and Kr in amorphous Si (a-Si) have shown that there is no thermal mobility at all at temperatures below the crystallization temperature (~ 800 K) [5]. Some irradiation-induced mobility may have occurred which might have led to an extra spread of about 0.6 nm on top of the straggling of 0.4 nm expected for 50 eV Kr implantation [3]. This small mobility explains the observation of an oscillating Kr concentration.

The maximum size of the agglomerates can also be inferred from HREM. The contrast will wash out if the average size of the agglomerates is larger than about 1 nm. This in agreement with the anomalous bond angle distortion observed by Raman spectroscopy and the very high Debye temperature ($\Theta_D > 250$ K) of the incorporated Kr observed by Mössbauer spectroscopy [3], which also indicates the formation of very small Kr agglomerates. Preliminary results of atomistic calculations indicate that $\Theta_D > 200$ K might be explained by assuming such a structure for Kr in a-Si.

The bending of the sample was monitored with an optical microscope. The sample shows a maximum bending of 160 μm at the centre, which corresponds to a curvature radius R of 253 mm. The stress in the film was calculated from the well-known Stoney equation [6] relating the substrate bending to a biaxial in-plane stress:

$$\sigma = \frac{E_s}{1-\nu} \frac{t_s^2}{6Rt_f} \qquad (1)$$

where E_s and ν are Young's modulus and Poisson's ratio respectively for the Si substrate, t is the thickness, R is the effective substrate radius of curvature, and the subscripts s and f refer to substrate and film respectively. It is assumed that a plane-strain situation exists and that the bending can be described as a linear elastic event without inelastic deformations. Further, all other elements in the stress tensor are assumed to be zero, including a possible shear stress at the sbustrate–film interface and a stress normal to the plane of the substrate–film. Although near the edge of the film a substantial change in the stress state might occur and localized normal and shear stresses are important for adhesion, these components of the stress tensor are neglected. Under these assumptions (using the elastic constants $c_{11} = 165.7$ GPa, $c_{44} = 79.6$ GPa and $\nu = 0.215$, $E_s = 2\mu(1+\nu) = 165.2$ GPa [7]), eqn. (1) yields a planar biaxial stress $\sigma_{xx} = \sigma_{yy} = \sigma = 0.34$ GPa. A more accurate formula relating the substrate bending to a planar stress has been proposed [8]; however, in the present case the stress calculated by the original Stoney equation turns out to be only 7% too high.

Wolfer [9] has derived an expression for the stress in a film containing a high concentration of pressurized bubbles. In our case the Kr atoms are probably distributed in the form of individual atoms or small clusters. This is not a serious problem, however, because Wolfer's expression remains correct if the word "bubble" is interpreted as an inclusion producing a local stress field at its surroudings. The stress field produced by such a "bubble" is, apart from a shear tensor, given by a hydrostatic stress σ_H, which for $R \leq r \leq_c$ is given by

$$\sigma_H = \frac{\bar{p}S}{1-S} + \frac{(p-\bar{p})\alpha S}{1-\alpha S} \qquad (2)$$

where p is the pressure inside a bubble of radius R, $\bar{p}$ is the average pressure of the bubbles in the material, S is the volume fraction of the bubbles, r is the length of the radius vector with origin in the bubble centre, $r_c = R/S^{1/3}$ is the linear size of the volume containing on the average one bubble and α is a function of shear and bulk modulus. Noordhuis and De Hosson [10] use these expressions for their analysis of the nucleation of martensite in Ne-implanted type 304 stainless steel. An important factor in the relation between the bubble pressure and the film stress forms the volume fraction S of the bubbles, which in our case, using a molar volume of 20 cm^{-3} mol^{-1} for Kr at pressures of the order of GPa [11], amounts approximately to $S = 8\%$. Follow-

ing the expressions given by Wolfer and applying $\bar{p} = p$, we find that an average hydrostatic pressure $\bar{p} =$ 3.9 GPa is necessary to produce a hydrostatic stress σ_H equal to 0.34 GPa. This presure is very high and is usually only observed for inert gases in high melting temperature materials [12].

It is of interest to see whether the high hydrostatic pressure can be related to the maximum stress that the solid can take before fracture will occur. Therefore microhardness measurements were carried out, resulting in a Vickers hardness value of 1159 kgf mm^{-2}. This corresponds to a yield stress of the a-Si films of $\sigma_Y{}^a = 3.86$ GPa and may be written in terms of the shear modulus $\mu^c = c_{44}$ of cyrstalline Si (c-Si) as $\sigma_Y{}^a = 0.048\mu^c$. This value is in agreement with the following consideration. Regard an amorphous material as consisting of an irregular disclination network [13, 14]. In contrast with a dislocation network the elastic energy stored in a disclination network would increase with increasing distance from a particular disclination, leading to a positive or negative curvature of the material. In order to compensate for this, assume that the network consists of positive and negative disclinations with a density ρ and a certain average distance $l = 1/\rho^{1/2}$ apart. Since radial distribution functions of amorphous materials in real space usually extends up to the fifth nearest neighbours with a certain correlation, the separation between the two disclinations in our supposed network is about $5b$, where b represent the magnitude of the Burgers vector. This implies a high disclination density of about 3×10^{17} m^{-2}. The yield stress of an amorphous material is now described as cutting of the disclination network by dislocations, *i.e.* it is related to opposing the line tension T as in the crystalline case: $\sigma_Y{}^a = 2T/bl$, where $T = \mu^c b^2 \ln(l/b)/4\pi$ [15]. Assuming that $l = 5b$, we find that $\sigma_Y{}^a = 0.051\mu^c$, *i.e.* about one twentieth of the shear modulus of c-Si. Indeed this is close to the experimentally determined value. This simple model ignores any self-energy of dislocations as well as splitting of disclinations. Further, b is taken to be constant although the physical picture will in fact suggest fluctuations in b due to the disclinations.

The question is whether we can make an estimate of the shear modulus μ^a of a-Si. A first-order approximation is to equate the theoretical yield stress and shear modulus of c-Si: $\sigma_Y{}^c = \mu^c$. Adopting this also for amorphous material, we can write $\sigma_Y{}^a = \mu^a = \frac{1}{20}\mu^c$. However, this is a lower bound value. Description of the local stress-displacement profile corresponding to an ideal fracture event by Frenkel [16] predicts, when applied to a-Si, a maximum theoretical stress $\sigma_Y{}^a \approx \lambda\mu^a/\pi a \approx 0.4\mu^a$, where λ is the interatomic distance and a the planar spacing. Taking $\lambda \approx a$, this yields $\mu^a \approx 0.1\mu^c$. At any rate the fracture stress will be greatly reduced by the lower elastic moduli in the amorphous case. In this sense it is quite instrumental to look at the Griffith fracture stress σ_F for brittle materials at which spontaneous fracture will occur when the magnitude of the crack extension and crack-resistant forces are equal [17]:

$$\sigma_F = \left(\frac{8\gamma\mu^a}{\pi d}\right)^{1/2} \tag{3}$$

where γ is the surface energy per unit area and d represents the diameter of the crack. If we take the fracture stress equal to the earlier found pressure in the "bubble", $\sigma_F = \bar{p} = 3.9$ GPa, $\gamma = 1.2$ J m^{-2} and the proposed reduction in the elastic constants, the largest stable crack diameter, *i.e.* size of the Kr inclusions, is ranging between 0.8 and 1.6 nm. In this analysis it is assumed that not extensive plastic deformation occurs upon crack propagation and that the surface free energy of a-Si is identical with the surface free energy of c-Si.

4. Conclusions

Thin Kr–Si films were produced by pulsed sputter deposition, yielding a Kr concentration of about 5 at.%. HREM experiments show that the film grown has an amorphous structure bearing an oscillating Kr concentration with period 1.3 nm, in accordance with the pulsation used for deposition. The maximum size of the Kr agglomerates is estimated to be 1 nm. The bending of the films was measured, yielding a curvature radius $R = 253$ nm, which corresponds to a planar biaxial stress of 0.34 GPa. The pressure of the Kr agglomerates was derived to be 3.9 GPa. The yield stress in the film was measured to be 3.86 GPa, *i.e.* about one twentieth of the shear modulus of c-Si. If we take a reasonable value for the shear modulus of a-Si, the size of the Kr agglomerates can be estimated on the basis of the Griffith fracture criterion, yielding 0.8–1.6 nm. Thus it is likely that the Kr pressure is limited by the fracture stress of a-Si.

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