Nanoindentation-induced pile-up in hydrogenated amorphous silicon

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Abstract. Nanoindentation-induced material extrusion around the nanoindent (pile-up) leads to an overestimation of elastic modulus, E, and nanohardness, H, when the test results are evaluated using the Oliver and Pharr method. Factors affecting the pile-up during testing are residual stresses in film and ratio of film and substrate mechanical properties. Nanoindentation of hydrogenated amorphous silicon (a-Si:H) films has been carried out with the aim to study the effect of residual compressive stress on the pile-up in this material. To distinguish the contribution of compressive stress to the appearance of pile-up ion implantation has been used as a tool, which reduces the compressive stress in a-Si:H. Scanning probe microscope has been used for the imaging of the indent and evaluation of the pile-up. The values of E and H have been obtained from the experimental load-displacement curves using depth profiling with Berkovich tip, which has created negligible pile-up. A sharper cube corner tip has been used to study the pile-up. It has been established that pile-up is determined by the material plasticity, when the compressive stress is below 200 MPa. The contribution of mechanical stress to the pile-up is essential for the stress as high, as about 500 MPa.

1. Introduction

The use of thin films and materials in small volumes in photonics, micro- and nanoelectronics and micro- and nano-electromechanical systems has created a strong interest in mechanical properties of thin films. The requirements for mechanical reliability and durability become more stringent with increasing the complexity of the systems and are particularly important for the devices used as sensors for environmental control and chemical and biological application.

Thin films of hydrogenated amorphous silicon (a-Si:H) have been used in some application fields as alternative to crystalline silicon, due to the relative ease and low cost preparation. Moreover, a-Si:H can be prepared at low temperatures, rendering it attractive for integration with biomaterials and biomedical applications. Thus, the engineering and control of the mechanical properties of a-Si:H films using appropriately varied film deposition conditions becomes an important issue.
Nanoindentation testing is a technique which can be used for assessment of the elastic and plastic properties of thin films. Using continuously recording indentation technique the values of elastic (Young’s) modulus, E, and nanohardness, H, can be obtained from the experimental load-displacement curves, which give the value of maximal load and the contact stiffness.

The value of projected contact area, A, can be calculated from the contact depth using the relationship, which is given by the calibrated area function. The calibration is usually conducted by the indentation of a standard sample with known mechanical parameters. In case when the mechanical properties of the studied material and the standard sample are different there might be error in the calculated contact area. For materials, which undergo plastic deformation there is pile-up at the edge of the contact with the indenter, which means that the actual contact area is larger, than the value calculated from the calibrated area function. Therefore, the employment of the Oliver and Pharr method in the case of pile-up leads to erroneous assessment of mechanical properties, and namely to an overestimation of E and H.

The primary material properties that are associated with the appearance of pile-up and determine its degree are residual stress and plasticity. It has been shown that pile-up takes place in thin films with compressive stress [2, 3]. Finite element modelling (FEM) has been used to examine the role of plasticity [4, 5] and it has been established that pile-up is significant in materials with a ratio of yield stress (the stress at which a material begins to deform plastically), Y, to elastic modulus, E, below 0.5. The lower Y/E, the more material is extruded by the indentation. In addition, it has been shown that the ratio of film and substrate hardness may also have an impact on pile-up, which typically takes place in the case of soft films on hard substrates [6-9]. As the most reported results are related to hard dielectric or soft metal films, the current knowledge is deficient on the experimental data for the pile-up induced by nanoindentation in thin semiconductor films. Moreover, information is lacking about the relative contribution of compressive stress and plasticity to pile-up.

The aim of the present work is to establish the degree of sensitivity of pile-up to the mechanical stress. To distinguish the contributions of compressive stress and Y/E to the appearance of pile-up ion implantation has been used as a tool, which reduces the compressive stress in a-Si:H, while keeping Y/E nearly constant. The values of yield stress and elastic modulus are established using Berkovich tip, which induces negligible pile-up and the employment of the Oliver and Pharr method is legitimate. A sharp cube corner tip is used for pile-up creation and evaluation.

2. Experimental procedure

The a-Si:H films were prepared by plasma-enhanced chemical vapour deposition (PECVD) using 10% silane diluted in hydrogen. The deposition experiments were carried out at a substrate temperature of 270°C and a gas pressure of 1 Torr. The film thickness was about 400 nm. Corning 7059 glass (elastic modulus 67.6 GPa, hardness 7.2 GPa) was used for substrates. Glass bars 0.3×3×30 mm³ were used as substrates for mechanical stress measurements. The hydrogen concentration in the material was about 15 at.%, determined by nuclear reaction analysis. Raman scattering spectroscopy indicated that the a-Si:H films were amorphous.

Si ion implantation was performed at room temperature without taking measures for sample cooling. The ion beam was normal to the surface. The implantations were carried out using Si ion energies of 160 keV. The implantation doses were in the range of $1.0 \times 10^{13} \text{cm}^{-2}$ - $1.0 \times 10^{15} \text{cm}^{-2}$.

The value of mechanical stress was determined by taking the difference in the substrate curvature with the film intact and after the film was removed by etching. The radius of curvature was obtained by measuring the change in angle of a He-Ne laser beam, reflected from the sample when the latter was moved laterally. The values of total stress were calculated using constants given in [10] and the expression:

$$\sigma_{tot} = E_s d_s R_{eff}^{-1}/[6(1-\nu_s)d_s],$$

where $\sigma_{tot}$ is negative for compressive stress, $E_s$, $\nu_s$ and $d_s$ are the Young’s modulus, Poisson’s ratio and thickness of substrate, respectively; $d_f$ is the film thickness; $R_{eff}^{-1} = (R^{-1} - R_o^{-1})$. R and $R_o$ are the radii of substrate curvature with and without the film, respectively.
The intrinsic stress was obtained by abstracting the thermal stress $\sigma_{th}$ from the total stress $\sigma_{tot}$.

$$\sigma_{th} = (\alpha_s - \alpha_f)(T_d - T_m)E_f/(1-\nu_f),$$

where $E_f$ and $\nu_f$ are the Young’s modulus and Poisson’s ratio of the film, $\alpha_s$ and $\alpha_f$ are the thermal coefficients of expansion for the substrate and the film, and $T_d$ and $T_m$ are the deposition and measurements temperatures, respectively. The stress in the studied a-Si:H films was compressive.

The present study utilized a TI 900 Triboindenter, Hysitron Inc. Nanoindentation testing was performed in quasi-static mode. The values of hardness and elastic modulus were established using diamond indenter with Berkovich tip (radius 170 nm). The maximum loads were in the range of 0.3 – 8.1 mN. The loading rates were in the range of 0.03 - 0.81 mN/s and cycle time was kept constant. The cycles were without hold time and with equal loading and unloading periods. For statistics the indentations tests were repeated 6 to 10 times in different locations of the samples. The standard deviations in the measurements were about 1.5 - 4 % of the respective means. The probe area function for Berkovich tip was regularly calibrated using a standard fused quartz sample, provided by Hysitron Inc. In addition, the projected contact area, $A$, was directly evaluated using scanning probe microscope (SPM). The difference between the values of $E$ and $H$ obtained using the calculated and measured values of $A$ was within the mentioned statistical error.

SPM integrated in the Triboindenter system was used for surface imaging after the indentation. The imaging was carried out with a tip velocity of 2 - 6 µm/s and a contact force setpoint of 1 µN. Cube corner tip with radius of about 55 nm was used for pile-up creation and imaging.

3. Experimental results and discussion

Figure 1 shows the SPM images of the indentations with Berkovich tip and cube corner tip for the as-deposited a-Si:H. The contact impression on a-Si:H obtained with Berkovich tip exhibits negligible pile-up, which suggests that the respective P-h curves can be used for elastic modulus and hardness evaluations following the approach of Oliver and Pharr [1]. This approach has been verified by direct measuring the indents area, using the SPM images of the indentations with various maximal loads.

Figure 1(b) shows that a large pile-up of a-Si:H appears for indentations by cube corner tip. Since the ratio of film and substrate hardness have an impact on pile-up in the case of soft films on hard substrates, to avoid the influence of the substrate, Corning 7059 glass was chosen as substrate, because its hardness of 7.2 GPa is lower than the hardness of 11-13 GPa [12-14] characteristic for silicon.

The data obtained from the P-h curves for thin films on substrates are composite values of elastic modulus, $E_{rc}$, and hardness, $H_c$, i.e. characteristic of the entire film/substrate system. The values of $E$ and $H$ of the a-Si:H films have been established using depth profiling of $E_{rc}$ and $H_c$, which
Figure 2. P-h curves of a series of indentations with different maximal loads up to 8.1 mN.

comprises a series of indentation tests with different maximal loads to achieve different maximal penetrations into the film (figure 2). Using this approach the dependencies of the composite values of elastic modulus $E_{rc}$ and hardness $H_c$ on the maximal displacement have been obtained. The extrapolation of these curves to the zero displacement [11], using second order polynomial fit, provides the values of $E$ and $H$ for the film (figure 3). The yield stress, $Y$, was estimated using the obtained value of $H$, and the eq. (31), page 112 in the Ref. [5]. The relationship is $H = 2.3Y$.

Figure 4 shows a schematic view of the cross-section of an indent and is used for the definition of the variables $h_b$ and $h_i$. The ratio of the mean height of the bows, $h_b$, to the depth of the impression, $h_i$, has been used for quantitative estimation of the effect of ion implantation on pile-up.

Figure 5 (a, b) shows the XZ plane cross-sections of the SPM images of the indentations with cube corner tip with equal maximal load of 0.6 mN. For the as-deposited a-Si:H film there is a significant vertical displacement of material at the edges of the contact impression. The indent in the implanted film is deeper in comparison with the as-deposited film, which reflects the increase in plasticity. However, the bows around the contact are lower in the implanted film. Both changes lead to a lower value of $h_b/h_i$ (see table 1), i.e. ion implantation leads to a decrease in the pile-up.

Figure 5. The XZ plane cross-sections of the SPM images of the indentations with cube corner tip of as-deposited (a) and implanted a-Si:H films.
Table 1 summarizes the effect of ion implantation on the mechanical properties, compressive stress and pile-up. E is calculated taking the value of 0.22 for the Poisson’s ratio [15]. The elastic modulus of 119 GPa of the as-prepared a-Si:H is lower than the elastic modulus reported for crystalline silicon (c-Si), 160-180 GPa [12, 13] and closer to that of the hydrogen-free silicon layers (a-Si) amorphised by high dose ion implantation, 127 - 145 GPa [12]. The obtained value of hardness of 12.3 GPa for the as-deposited a-Si:H film is comparable to the hardness of c-Si (11.4 – 13.0 GPa) [12, 13, 14] and is higher, than the hardness of hydrogen-free a-Si prepared by ion implantation-induced amorphization of c-Si or by a deposition technique (9.0 - 11.5 GPa) [12, 16, 17]. The observed change in the elastic properties of the implanted a-Si:H is similar to the effect of ion implantation on the mechanical properties of c-Si [18] and can be associated with the induced increase in the network disorder [19]. It can be suggested that the decrease in E is related to the structural change in the implanted a-Si:H, such as the implantation-induced increase in the Si-Si bond angle deviations.

Table 1. Elastic modulus, E, indentation hardness, H, yield stress to elastic modulus ratio, Y/E, compressive stress, σ, and pile-up parameter, h_b/h_i of the as-deposited and ion implanted a-Si:H.

| Ion dose (cm⁻²) | none | 1x10¹³ | 1x10¹⁴ | 1x10¹⁵ |
|----------------|------|--------|--------|--------|
| E (GPa)        | 119 ± 3 | 115 ± 3 | 108 ± 3 | 101 ± 3 |
| H (GPa)        | 12.3 ± 0.35 | 11.6 ± 0.35 | 10.1 ± 0.35 | 9.4 ± 0.35 |
| Y/E            | 0.045 ± 0.002 | 0.044 ± 0.002 | 0.041 ± 0.002 | 0.041 ± 0.002 |
| σ (MPa)        | 766 ± 20 | 658 ± 20 | 138 ± 10 | 31 ± 5 |
| h_b/h_i        | 0.33 ± 0.02 | 0.25 ± 0.01 | 0.20 ± 0.01 | 0.19 ± 0.01 |

Si ion implantation of a-Si:H leads to a decrease in hardness to the values typical for the hydrogen-free a-Si (Table 1). This change is apparently related to the implantation-induced damage and reflects the mechanism of plastic deformation of a-Si:H. Two mechanisms of plastic deformation are reported for silicon, namely, phase transformation and plastic flow [16, 19-21]. The main indicator for the operation of phase transformation during nanoindentation is the appearance of the discontinuities (kinks or pop-outs) in the P-h curves. Their absence in the obtained P-h curves suggests that the nanomechanical testing performed in the present study does not induce phase transformation, i.e. the plastic deformation of a-Si:H is accomplished by plastic flow. Plastic flow is generally considered to be associated with the presence of a high density of dangling bonds and any change in this density is expected to affect the material hardness. Ion implantation leads to an increase in the density of dangling bonds by causing atom displacements in the target and this is the origin of the decrease in the nanohardness of a-Si:H.

The decrease in both E and H due to the ion implantation, keeps the ratio Y/E almost constant for the ion doses used in this work. Having in mind the measurement accuracy, the mean value of Y/E of about 0.43 can be considered as typical for both as-deposited and implanted a-Si:H film. This makes it possible to distinguish the contribution of compressive stress to the pile-up.

The decrease in the compressive stress due to implantation is substantial (table 1). The compressive stress in a-Si:H is associated with the presence of clustered hydrogen in the silicon matrix. The ion implantation leads to a decrease in the relative amount of clustered hydrogen and in this way reduces the compressive stress [22]. The residual stress becomes negligible at the highest Si ion dose of 1x10¹⁵ cm⁻². On the other hand, the pile-up characteristic h_b/h_i decreases to 0.20 for the ion dose of 1x10¹⁴ cm⁻² and further increase in the ion dose leads to a negligible change in h_b/h_i , i.e. there is a saturation trend. It can be suggested that the value of h_b/h_i of about 0.20 is related to the pile-up associated with the material plasticity and corresponds to the value of Y/E of about 0.43. The obtained results point out that for a-Si:H the effect of the residual compressive stress is essential for strongly stressed films (σ ≥ 500 MPa) and is additive to the pile-up related to the plasticity. Since the value of compressive
stress in a-Si:H depends strongly on the deposition conditions [23] the comparison of nanomechanical properties of various samples cannot be straightforward because of the different degree of pile-up.

4. Conclusion
The sensitivity of pile-up to the mechanical stress in a-Si:H films has been studied. Ion implantation was used as a tool to decrease the compressive stress in the films. The values of $E$ and $H$ decreased with the ion dose, while the value of $Y/E$ remained nearly constant. Using this effect of ion implantation it was possible to distinguish the contribution of mechanical stress to pile-up. It has been established that for a-Si:H the impact of the residual compressive stress on the pile-up is essential for strongly stressed films and is additive to the pile-up related to the plasticity.

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