Narrowing of the Boolchand intermediate phase window for amorphous hydrogenated silicon carbide

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ABSTRACT

Intermediate phases represent the so called "sweet spot" in amorphous material systems where the bond stretching and bond bending constraint forces are equally balanced by the total degrees of freedom in the system. They are sometimes also referred to as "Boolchand" phases in recognition of the seminal contributions of Dr. Punit Boolchand to the study of these materials. In a prior publication (King et al., *J. Non-Cryst. Solids* 379 (2013) 67), we presented possible evidence for the existance of an intermediate (i.e. "Boolchand") phase in amorphous hydrogenated silicon carbide (a-SiC:H) with a wide range in mean atomic coordination ($\langle r \rangle$ = 2.4 − 2.7). Support for such a wide phase window was based primarily on a correlation between the post plasma deposition bi-axial film stress and $\langle r \rangle$. However, we demonstrate in the present article that the apparent width of the Boolchand intermediate phase window in the prior study was inflated due to two competing film stress contributions, and that the true range in $\langle r \rangle$ for the phase window is substantially narrower. Specifically, opposing tensile and compressive film stress components were identified to arise during the plasma enhanced chemical vapor deposition (PECVD) of a-SiC:H. The tensile film stress component was attributed to film/substrate thermal contraction mismatch on cooling from the deposition temperature, while the compressive stress component was attributed to ion bombardment of the a-SiC:H growth surface during PECVD. In the prior study, the energy of the ions during PECVD was primarily modulated by the addition of a low frequency bias to the plasma and was intentionally utilized to produce films with varying compressive stress and $\langle r \rangle$. In the present study, the low frequency bias was removed from the PECVD of a-SiC:H and instead the deposition pressure was varied to produce films with varying $\langle r \rangle$ and exclusively tensile stress. Through detailed analysis of the tensile bi-axial film stress and Young's modulus dependence on $\langle r \rangle$, we found conclusive evidence that the film-substrate thermal contraction mismatch was the dominant film stress component in this case and that the magnitidue of the tensile stress was purely due to rigidity percolation in the a-SiC:H film. We therefore conclude that in our previous study the balance of the tensile and compressive stress components resulted in the deceptive appearance of a potentially wide Boolchand intermediate phase window for a-SiC:H. Based on the a-SiC:H films generated in the present study where only the tensile stress component was significant, we have found the window for a possible intermediate phase to be greatly narrowed at $\Delta \langle r \rangle \leq 0.05$.

1. Introduction

Intermediate phases [1–4] are one of the many interesting discoveries arising from the Phillips-Thorpe theory of topological constraints for amorphous materials [5, 6]. Such intermediate amorphous phases ideally represent the so called "sweet spot" where the bond stretching and bond bending constraint forces are equally balanced by the total degrees of freedom in the system [7, 8]. Although their exact structural origin or signature is a matter of significant debate [9, 10], amorphous materials with intermediate phase compositions are found

to exhibit various attractive properties including self organization [11], thermal reversibility [12], negligible aging effects [13], lack of internal stress formation [14–16], and low defect densities [17]. The formation of intermediate phases have additionally been linked to a variety of other important scientific phenomena including high temperature superconductivity [18], protein folding [19], and computational phase transformations [20]. Intermediate phases are sometimes also referred to as "Boolchand" phases [21] in recognition of the seminal contributions of Dr. Punit Boolchand to experimentally isolate and demonstrate the unique properties of intermediate phase materials [22, 23].

Based on the Phillips-Thorpe theory, the point of isostaticity that defines the formation of an intermediate Boolchand phase occurs at a critical mean atomic coordination ($\langle r \rangle$) below which an under-constrained and flexible phase exists and above which an over-constrained and rigid phase exists [6]. Unfortunately, the compositional window or range in $\langle r \rangle$ experimentally observed for intermediate phases in amorphous systems is typically quite small [24–26] with $\Delta\langle r \rangle$ typically ranging from as low as 0.008 for the GeSeI system to as high as 0.21 for the GeAsSe system [7]. However, in a previous study of plasma enhanced chemically vapor deposited (PECVD) amorphous hydrogenated silicon carbide (a-SiC:H) thin films, we presented possible evidence for a much wider intermediate phase window of $\langle r \rangle$ = 2.4–2.7 ($\Delta\langle r \rangle$ = 0.3). This was based primarily on a correlation between the a-SiC:H post deposition bi-axial film stress and $\langle r \rangle$ [27]. Specifically, the compressive film stress for the a-SiC:H films was observed to decrease with decreasing $\langle r \rangle$ and approach near neutral values at $\langle r \rangle$ = 2.7. The attribution of the near zero stress observed at $\langle r \rangle$ = 2.4–2.7 to an intermediate phase was tentative though due to the known presence of counteracting tensile and compressive stress components to the measured film stress that could effectively negate one another and thus falsely suggest the presence of an isostatic phase [27].

In the present study, we have generated a new series of a-SiC:H films where the plasma deposition process has been intentionally modified such that only the tensile stress contribution is significantly present, thus allowing the true range of a possible intermediate phase window to be more clearly observed. Specifically, the low frequency bias previously applied during plasma deposition was removed from the present process [28]. This bias is typically utilized to enhance ion bombardment of the film [29], increase mass density and $\langle r \rangle$ [30], and impart a compressive stress to the growing film [31]. The removal of the low frequency bias significantly reduced the compressive stress contribution to the a-SiC:H films leaving only the tensile stress arising from the mismatch in coefficient of thermal expansion (CTE) between the Si substrate and the a-SiC:H films [32]. As we will show, we find that for such tensile a-SiC:H films the apparent intermediate phase window is greatly reduced to $\Delta\langle r \rangle$ < 0.05.

2. Experimental

2.1. Film deposition

The details of the a-SiC:H film deposition have been provided previously [33, 34]. Briefly, all a-SiC:H films analyzed in this study were deposited using a standard commercially available parallel plate capacitance PECVD tool and various mixtures of methylated silanes diluted in gases such as H_2 or He [35]. All films were deposited on 300 mm diameter, double-side polished (001) silicon substrates at temperatures on the order of 400 °C [36]. The hydrogen content for the a-SiC:H films was further controlled by adjusting the deposition pressure, high (13.56 MHz) and low (200–400 kHz) frequency applied power, and reactant/diluent ratio [37]. For the a-SiC:H films examined in the present study, the low frequency bias was intentionally set to zero in order to minimize the energy of the ions bombarding the a-SiC:H films during growth and in turn to minimize the compressive stress component to the final a-SiC:H bi-axial film stress [31]. The film thickness and refractive index for the a-SiC:H films were determined using a variable angle spectroscopic ellipsometer (VASE) [38].

2.2. Elemental composition and mean coordination ($\langle r \rangle$)

The elemental composition for the a-SiC:H films was determined by combined nuclear reaction analysis (NRA) and Rutherford backscattering spectroscopy (RBS) measurements performed at the Albany Dynamitron Accelerator Laboratory. This analysis has been described in detail previously [39]. Briefly, the H analysis was performed using the ^{15}N nuclear reaction method and the C and O contents were determined

using deuteron nuclear reactions. Rutherford backscattering spectrometry (RBS) with 2 MeV [4]He was used to determine the Si content. With the film's absolute H, C, O, and Si composition, parameter free simulations of the full RBS spectra were performed using the program RUMP [40] to validate the elemental analysis. As a consistency check, the mass density determined for the a-SiC:H films by NRA-RBS were compared to values independently determined by previously described x-ray reflectivity (XRR) measurements [41]. The two techniques were found to be in agreement to within ± 0.1 g/cm^3.

The mean atomic coordination $\langle r \rangle$ for the a-SiC:H films was directly calculated using the combined NRA-RBS elemental analysis according to the following expression [42]:

$$\langle r \rangle = (4[\text{Si}] + 4[\text{C}] + 2[\text{O}] + [\text{H}])/([\text{Si}] + [\text{C}] + [\text{O}] + [\text{H}]) \qquad (1)$$

The coordination for carbon was assumed to be 4-fold sp^3 in all cases based on previous nuclear magnetic resonance (NMR) measurements where evidence of some 3-fold sp^2 carbon was found only for a-SiC:H films with much lower mass density than those produced in the present study [43].

2.3. Film stress and mechanical properties

The a-SiC:H bi-axial film stress was determined from wafer curvature measurements performed immediately post deposition using a previously described laser deflection method [44]. The post deposition film stress was calculated from the measured wafer curvature using Stoney's formula and the optically determined film thickness which ranged from 300 to 700 nm [45]. The hardness and indentation modulus for the a-SiC:H films were determined by nanoindentation measurements using a Nano XP nanoindenter with a Berkovich diamond tip (radius ≅ 100 nm) [46]. The samples were loaded in continuous stiffness mode and the hardness and modulus were calculated by averaging fifteen indents [46, 47]. The indentation modulus (M) was converted to Young's modulus (E) according to the relation E = M(1 − ν^2) where ν was taken to be 0.25 based on previous SAW measurements of related a-SiC:H films where ν = 0.25 ± 0.05 was determined for $\langle r \rangle$ = 2.5–3.2 [42].

3. Results and discussion

3.1. Mechanical properties

Fig. 1 presents the nanoindentation Young's modulus and hardness for the a-SiC:H thin films as a function of their mean coordination $\langle r \rangle$ determined from the combined NRA-RBS measurements. Included in Fig. 1 are data points from both the current investigation (open triangles) and the previous publication (open diamonds) [27]. As can be seen, the combined data cleanly fall within the same distribution indicating no systematic offsets between the NRA-RBS and nanoindentation measurements. Also included in Fig. 1 is a vertical dashed line indicating the critical mean atomic coordination ($\langle r \rangle_c$) for the isostatic point where the bond stretching and bond bending forces in a-SiC:H are just balanced by the total degrees of freedom. For tetrahedrally coordinated systems (such as a-SiC:H), $\langle r \rangle_c$ has been determined to be 2.4 as shown in Fig. 1 [6, 48].

Below $\langle r \rangle_c$, amorphous materials are considered to be mechanically underconstrained and flexible [49, 50]. Most importantly, the Phillips-Thorpe theory predicts that mechanical properties such as Young's modulus and hardness should be invariant with $\langle r \rangle$ when $\langle r \rangle < \langle r \rangle_c$. As shown in Fig. 1, this is clearly observed for the a-SiC:H films generated in our prior study. In contrast, materials are considered to be mechanically overconstrained and stressed rigid when $\langle r \rangle > \langle r \rangle_c$ [6, 48]. In this case, bond depleted network numerical simulations motivated by the Phillips-Thorpe theory indicate that mechanical properties such as Young's modulus and hardness should increase with increasing $\langle r \rangle$ above $\langle r \rangle_c$ to the 3/2 power (i.e. $\propto (\langle r \rangle - \langle r \rangle_c)^{3/2}$) [51, 52]. The grey