



Influence of hydrogen content and network connectivity on the coefficient of thermal expansion and thermal stability for a-SiC:H thin films



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ARTICLE INFO

Article history:

Received 30 August 2013

Received in revised form 5 February 2014

Available online 12 March 2014

Keywords:

Silicon carbide;

Coefficient of thermal expansion;

Plasma enhanced chemical vapor deposition;

Low-*k*;

Constraint theory

ABSTRACT

Thin films of a-SiC:H are of interest for numerous applications in optoelectronic, nanoelectronic, and nanoelectromechanical devices due to a large optical band gap and excellent chemical inertness. In many cases, a low coefficient of thermal expansion (CTE) and high temperature stability are also desired. In this regard, we report an investigation of the influence of hydrogen content and average bond coordination ($\langle r \rangle$) on the thermal stability and CTE of a-SiC:H thin films deposited by plasma enhanced chemical vapor deposition. The a-SiC:H hydrogen content determined by combined nuclear reaction analysis and Rutherford backscattering measurements (NRA-RBS) was skewed from 25 to 60% resulting in films with $\langle r \rangle$ ranging from 2.0 up to 3.2. We show that increased hydrogen content is accompanied by changes in the thermal stability and CTE for the a-SiC:H films. The most dramatic changes were observed to occur for films with hydrogen content >45% where $\langle r \rangle$ is near the critical coordination number ($\langle r \rangle_c$) that delineates over and under constrained materials. For a-SiC:H films above $\langle r \rangle_c$, relatively little change was observed in CTE with $\langle r \rangle$. However for films near or below $\langle r \rangle_c$, CTE was observed to increase with decreasing $\langle r \rangle$ and significant hydrogen loss was observed after the annealing measurements.

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1. Introduction

Hydrogenated amorphous silicon carbide (a-SiC:H) is a material with excellent material properties that makes it of interest for use in numerous optoelectronic [1,2], biomedical [3,4], nanoelectronic [5,6], tribological [7,8], and nanoelectromechanical [9,10] devices. Specific applications include use as an amorphous semiconductor [11–13], a surface passivation layer [14], a hermetic moisture or metal diffusion barrier [15–18], a corrosion and wear resistant protective coating [19–22], an insulating intermetal dielectric [23,24], an etch stop [25–27], and an x-ray hard mask [28,29]. In addition, a-SiC:H offers the added ability to tune the physical properties via varying the Si/C ratio or the total hydrogen content [30–32]. The former allows the realization of materials with properties spanning those of a-Si and a-C [33–37] while the latter allows the preparation of materials with a still wider range of properties [32,38–41].

In many of the above applications, a mix of material properties sometimes at disparate extremes is highly desired. One example would be the use of a-SiC:H as a low dielectric constant (i.e. low-*k*) material in

nanoelectronic metal interconnect structures [42] where a low dielectric constant is desired in combination with a high Young's modulus and low coefficient of thermal expansion (CTE) [43]. The low dielectric constant is desired to reduce resistance–capacitance delays in the metal interconnect whereas a low CTE and high elastic modulus is needed to minimize thermally generated strains and to provide sufficient rigidity to survive downstream processing and packaging processes [42–45]. These requirements are at odds with one another as low dielectric constants are typically achieved via incorporation of significant amounts of hydrogen that disrupts the Si–C network bonding [46,47], whereas a high modulus and low CTE are typically achieved at low hydrogen content and high Si–C network connectivity [40,48].

In light of the above conflicting requirements for a-SiC:H in low-*k* dielectric applications, we have elected to perform a detailed investigation of the thermal–mechanical properties of plasma enhanced-chemically vapor deposited (PECVD) a-SiC:H films as a function of hydrogen content and network connectivity. In previous studies [40,46], we have demonstrated that increased hydrogen content has a significant influence on the a-SiC:H network connectivity and properties such as Young's modulus, hardness, and thermal conductivity. In this study, we have specifically chosen to investigate the thermal stability and both the in-plane and out-of-plane CTE for a-SiC:H materials with varying

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hydrogen content and average coordination ($\langle r \rangle$). In contrast to the previous studies, we find that hydrogen content has a negligible influence on CTE and thermal stability for films where $\langle r \rangle$ is greater than the critical coordination number ($\langle r \rangle_c$) predicted by bond constraint/percolation theory. For $\langle r \rangle < \langle r \rangle_c$, we find that CTE increases significantly and the a-SiC:H films become increasingly thermally unstable as exhibited by significant changes in the film thickness and the loss of hydrogen after extended annealing at 400 °C (note this is substantially less than the melting point of single crystalline SiC ($T_{\text{melt}} \cong 2800$ °C [49])). For $\langle r \rangle > \langle r \rangle_c$, the combined in-plane and out-of-plane CTE measurements were found to be invariant with $\langle r \rangle$ and yield similar results confirming the expected isotropic properties for the as deposited a-SiC:H films.

2. Experimental

2.1. Film deposition

All the a-SiC:H films analyzed in this study were deposited using standard commercially available parallel plate capacitance PECVD tools and various silane- and methylsilane-like sources diluted in gases such as H₂ or He. All the films were deposited on 300 mm diameter, double-sided polished (100) silicon substrates. The details of the a-SiC:H deposition have been provided previously [46,47,50]. Briefly, most films were deposited at temperatures on the order of 400 °C, however, one highly porous film (a-SiC:H#1) was deposited at a lower temperature of 250 °C. For a-SiC:H#1, an organic pore building precursor (i.e. “porogen”) was intentionally added to the deposition process to facilitate the creation of significant levels of interconnected nanopores in the a-SiC:H film and to produce an ultra low-*k* a-SiC:H film [38]. In this case, the porogen was removed post-deposition using an industry standard electron beam cure at ~400 °C [51]. 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.

Film thickness and refractive index were determined using a J. A. Woollam variable angle spectroscopic ellipsometer (VASE) [52]. The a-SiC:H film stress immediately post-deposition was calculated using Stoney's formula and the optically determined film thickness and change in Si wafer curvature measured using a laser deflection method [53,54]. The percent porosity for these materials was determined by ellipsometric porosimetry (EP) measurements using toluene as the solvent [55–57]. The Young's modulus and hardness of the a-SiC:H films was determined by nano-indentation as previously described [58]. Table 1 summarizes some of the key material properties for the a-SiC:H films investigated in this study and that have been previously reported [46,47,50].

Table 1
Summary of select material properties for PECVD a-SiC:H films investigated in this study. ND = Not Detected.

Film	RBS C/Si	% Porosity	Stress (MPa)
a-SiC:H#1	5.0	<12	50
a-SiC:H#2	3.0	<2	10
a-SiC:H#3	1.1	ND	20
a-SiC:H#4	1.1	ND	60
a-SiC:H#5	1.5	ND	0
a-SiC:H#6	1.2	ND	−52
a-SiC:H#7	1.1	ND	−94
a-SiC:H#8	1.1	ND	−182
a-SiC:H#9	1.1	ND	−140
a-SiC:H#10	1.1	ND	−425
a-SiC:H#11	1.05	ND	−400
a-SiC:H#12	1.0	ND	−1100

2.2. In-plane CTE

The in-plane CTE for the a-SiC:H films was measured using a Frontier Semiconductor TC900 laser stress measurement system. Specifically, this tool was utilized to monitor changes in the a-SiC:H/Si wafer curvature as a function temperature using a laser deflection system previously described [59]. The wafer curvature is directly proportional to the intrinsic stress in the a-SiC:H film according to Stoney's formula [60]:

$$\sigma_f = E_s h_s^2 \Delta K / 6h_f \quad (1)$$

where σ_f is the biaxial film stress, E_s is the biaxial modulus of the Si substrate, h_s is the Si substrate thickness, h_f is the film thickness and ΔK is the change in substrate curvature after deposition of the a-SiC:H film. The value of σ_f post-deposition is the sum of thermally generated stresses (σ_t) and intrinsic stresses generated during the deposition process (σ_i) [58]. The thermally generated stress σ_t is a result of the mismatch in thermal contraction between the a-SiC:H film and the Si substrate on cooling from the deposition temperature. The intrinsic stress σ_i is the result of strained bonds formed in the film due to either un-optimized bond orientation or strain imparted to the film by ion bombardment during the plasma deposition process. On heating, the radius of curvature of the a-SiC:H/Si wafer will change with temperature (T) as a result of changes in the a-SiC:H film stress due to changes in the σ_t component. In this case, the CTE of the film (α_f) may be determined using the following relation [61]:

$$\partial \sigma_f / \partial T = [E_f / (1 - \nu_f)] (\alpha_s - \alpha_f) \quad (2)$$

where E_f and ν_f are respectively Young's modulus and Poisson's ratio for the a-SiC:H film, and α_s is the CTE for the Si substrate. For the experiments described here, the change in radius of curvature while heating from 23 to 400 °C in a $<10^{-5}$ Torr vacuum was measured using 500 nm thick a-SiC:H films deposited on Si. The maximum temperature of 400 °C was selected as this was the deposition/curing temperature for the films and is generally the maximum temperature allowed in low-*k*/Cu interconnect fabrication [54]. The heating rate was 5 °C/min and the cooling rate was approximately 10 °C/min. The samples remained at the target temperature of 400 °C for 5 min before cooling. The radius of curvature was monitored on heating and cooling for two cycles. Linear regression analysis was utilized to determine $\delta \sigma_f / \delta T$ over the temperature range of approximately 50–300 °C. To calculate the CTE of the a-SiC:H films, the CTE of the Si substrate was taken to be 2.6 °C/ppm and the a-SiC:H Young's modulus values previously determined by nanoindentation [58] were utilized. The Poisson's ratios for the a-SiC:H films were assumed based on previously reported measurements on identical or similar samples [21,62,63]. Specifically, the Poisson's ratio for a-SiC:H#1 and 2 was taken to be 0.33 ± 0.03 based on prior Brillouin light scattering measurements of identical samples [62]. For a-SiC:H#3–12, the Poisson's ratio was assumed to be 0.25 ± 0.03 based on prior measurements by Khakhani [21] and Cros [63] for a-SiC:H films of similar stoichiometry and hydrogen content.

2.3. Out-of-plane CTE

The out-of-plane CTE for identical 100 nm a-SiC:H films deposited on Si was determined by x-ray reflectivity (XRR) thickness measurements performed between room temperature and 400 °C. The details of these measurements have been described previously [64,65]. Briefly, the XRR measurements were carried out on a Bruker D8 Discover diffractometer (Cu K α radiation, $\lambda = 0.15418$ nm) equipped with a DHS 900 domed hot stage attachment. The temperature of the hot stage was controlled via a Paar Physica TCU 150 temperature control unit with N₂ gas continuously flowing through the dome. The samples were heated from the back through thermal contact with the hot

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