Photoacoustic measurements on thermal properties of hydrogenated amorphous carbon films: the effect of hydrogen dilution

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Abstract. Thermal properties of hydrogenated amorphous carbon (a-C:H) thin-films are measured using an ultrafast optical pump-probe technique. The a-C:H samples were grown in a home-built direct-current (DC) plasma enhanced chemical vapor deposition (PECVD) system with varying hydrogen (H2) diluents to methane (CH4) flow-rate ratios. Thermal diffusivities of samples are extracted by comparing thermoreflectance measurements with numerical calculations so that thermal conductivities (κ) can be determined. Although the dependence of thermal property on H2 dilution was not significant, our films show lower κ (0.10-0.15 W/mK ± 20%) compared to the results of previous studies.

1. Introduction
Hydrogenated amorphous carbon (a-C:H) is a member of diamond-like carbon (DLC) materials that have mechanical and thermal properties suitable for applications in microelectromechanical systems (MEMS) and nanoscale devices such as thermal actuators, micro-coolers, piezoresistive sensors, and so on.[1] To design such structures it is crucial to understand their thermal characteristics especially when they are subject to large heat loads or frequent temperature changes. While previous studies [2-4] show that thermal conductivities of certain a-C:H thin-films are in the range of 0.20-1.4 W/mK, these properties are known to be dependent on the fabrication process that results in different configuration of atomic structures such as crystallinity, hydrogen content in the film and sp2-to-sp3 bonding ratios. For this reason investigations on the thermophysics of the carbon material have been vigorously performed for various regimes of a-C:H.

In the present study the pump-probe technique was employed to determine thermal properties of a-C:H thin-films grown by plasma enhanced chemical vapor deposition (PECVD) with varying hydrogen (H2) diluents to methane (CH4) flow-rate ratios. The ultrafast optical pump-probe technique provides a contact-free and nondestructive way to evaluate mechanical and thermal characteristics of multilayers in nanometer-scale.[5,6] The measured thermoreflectance signals were analyzed using a computational model so that thermal diffusivities of films were yielded to see if the different diluents ratio affects the material properties.

2. Experimental
The a-C:H samples were deposited on single crystal silicon (Si) wafer substrates in a home-built
Table 1. Film characteristics.

| Sample # | Diluents-to-methane ratio | Film Thickness (nm) | Hydrogen content (%) | $sp^2$ carbon content (%) |
|----------|--------------------------|--------------------|----------------------|--------------------------|
| 1        | 1:1                      | 386                | 8.0                  | 23.8                     |
| 2        | 1:2                      | 470                | 4.0                  | 23.8                     |
| 3        | 1:3                      | 490                | 3.0                  | 17.7                     |
| 4        | 1:4                      | 560                | 5.3                  | 26.1                     |

direct-current (DC) PECVD system. The deposition time was fixed at 4 hours with a constant DC power of 6.7 W. The set consists of films deposited from the discharge of pure CH$_4$ diluted with H$_2$ such that the H$_2$-to-CH$_4$ flow-rate ratios varied from 1:1 to 1:4. The deposition temperature, pressure and CH$_4$ flow-rate were fixed at 100 °C, 0.2 mbar and 20 sccm, respectively.

The film thickness and Tauc gap, $E_g$ were measured from the optical transmission spectra of the films obtained using a Jasco UV-Vis-NIR 3102-PC double beam spectrophotometer scanned within a scanning range of 190 to 2500 nm. The spectra were fitted using MATLAB 7.0 developed by Suganthi et al.[7] Fourier Transform Infrared (FTIR) transmission spectra were done with Perkin Elmer 2000 FTIR spectrometer used in transmission mode in the range 400 to 4000 cm$^{-1}$ to determine the bonded hydrogen content (H%) of the films and to identify the $sp^2$ hybridization of C and CH bonds as well as other possible bonds that could appear due to the presence of hydrogen. The film characteristics are summarized in table 1.

After the sample fabrication, surfaces were coated with a thin layer (~30 nm) of aluminum in an e-beam evaporator (Edwards Auto 500) for the picosecond ultrasonics measurements. The DC voltage applied to a tungsten filament is 4.7 KV, and the current level was set to 25 mA to obtain a deposition rate of 0.15 nm/s. During the process the chamber pressure was maintained at $3 \times 10^{-6}$ Torr.

The time-resolved thermoreflectance signals were measured using the ultrafast optical pump-probe technique.[6] A femtosecond laser system (Millenia Pro and Tsunami, Spectra-physics) lasing at the beam wavelength of 780 nm and the full width at half maximum (FWHM) pulse duration of 120 fs was employed. The pulse repetition rate was 80 MHz. It was then split into the pump-beam, which is modulated at 100 kHz by an acousto-optic modulator (AOM, IntraAction Corp. AOM-405) to heat up the sample, and the probe-beam to monitor the reflectance change induced by the temperature rise. The intensity ratio of the two beams divided by a polarized-beamsplitter and a half-wave plate was 10 to 1. The transient response of thermoreflectance at a specific time-delay with respect to the application of pump-pulse was detected using a computer-controlled delay-line on which a retroreflector was installed. The maximum time-delay of the motorized stage was 1 ns, and the temporal resolution was set to 4 ps/pts in the present study. The probe-pulse was reflected by the Al-coated a-C:H sample mounted on an xyz-stage, and then collected by a photodetector (Thorlabs PDA36A) connected to a lock-in amplifier (Stanford Research SR803).

3. Data analysis

Curve-fittings have been performed with the measurement data to derive the thermal diffusivity ($\alpha$) following the model developed by Paddock and Eesley.[8] The one-dimensional heat conduction equation in a single-layer sample is:

$$\frac{\partial T(x,t)}{\partial t} = \alpha \frac{\partial^2 T(x,t)}{\partial x^2} + \frac{I(1-R)\beta e^{-\beta t} e^{-(t/\tau)^2}}{C}$$  \hspace{1cm} (1)

where $T$ is the sample temperature, $x$ is the distance normal to the sample surface, $t$ is the time-delay with respect to the pump-pulse application, $C$ is the heat capacity per unit volume, $R$ is the reflectivity,
Figure 1. (Color online) The thermoreflectance measurement results on α-C:H samples.

$I$ is the pump-intensity, $\beta$ is the absorptivity per unit length, and $\tau$ is the pump-pulse width of a Gaussian shape. Therefore, the shape of normalized solution depends on $\alpha$ of the α-C:H film and the absorptivity of Al-coat ($\beta$). In this study the best fitting is obtained with $\beta=105 \, \mu m^{-1}$, which is close to the theoretical value for Al.

4. Results and discussion

Figure 1 shows the optical pump-probe reflectivity data from the four α-C:H samples. It is observed that the heat from the pump-pulse takes 9 ps approximately ($\lambda = \sqrt{D\tau}$, where $\lambda$ is the thermal diffusion length (30 nm) and $D$ is the thermal diffusivity of Al ($9.75 \times 10^{-5} \, m^2/s$)) to diffuse into the Al layer, and it propagates in the carbon material afterwards. Based upon the aforementioned methods, thermal diffusivities are extracted and thermal conductivities ($\kappa$) are also calculated using the relationship $\kappa = \alpha C$. The density of film and specific heat capacity were taken from representative values of 2.4 g/cm$^3$[3] and 1.04 J/gK,[4] respectively. Results are summarized in table 2.

While the results indicate overall thermal conductivities of 0.10-0.15 W/mK within 20\% uncertainty, no significant dependence on the dilution ratio are observed. It can be explained by the general agreement that the H content has minor influence on the mechanical and thermal properties of the film,[3,4] but it is also because of the small variation of hydrogen content (3.0–8.0 \%) and $sp^2$ carbon content (17.7–26.1 \%), which do not change linearly with the flow-rate ratio. It is interesting,

| Sample # | $\alpha$ (mm$^2$/s) | $\kappa$ (W/mK) |
|----------|---------------------|-----------------|
| 1        | 0.04                | 0.10            |
| 2        | 0.06                | 0.15            |
| 3        | 0.06                | 0.15            |
| 4        | 0.05                | 0.12            |
however, that our films show relatively lower $\kappa$ compared to those of the previous investigations. For example, the lowest conductivities in Bullen et al.[2] and Shamsa et al.[3] are 0.20 W/mK for their remote-plasma chemical vapor deposition (RPCVD)-grown sample and polymer-like $a$-C:H (PLCH), respectively. Considering the increasing trend of $\kappa$ with respect to the film density[2-4], it is inferred that the current fabrication technique produces softer films, which will be clarified by photoacoustic characterization (broadband guided-wave technique[5]) in near future.

5. Conclusion

Thermal properties ($\alpha$ and $\kappa$) of $a$-C:H samples prepared by DC PECVD with varying H$_2$-to-CH$_4$ flow-rate ratios are determined from the thermoreflectance measurements. Although no obvious dependence of thermophysical characteristics on the flow-rate ratio is observed, our film-growth method results in relatively lower thermal conductivities (0.10-0.15 W/mK ± 20%) compared to those of the existing studies.

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