Sains Malaysiana 40(1)(2011): 59–62

Optical Constants and Electronic Transition in Hydrogenated Silicon (Si:H) Thin Films Deposited by Layer-by-Layer (LBL) Deposition Technique

(Pemalar Optik dan Peralihan Elektronik dalam Filem Nipis Silikon Terhidrogen (Si:H) disediakan melalui Teknik Mendapan Lapisan Demi Lapisan)

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ABSTRACT

Optical constants derived from optical transmission (T) and reflectance (R) spectra in the wavelength range of 220 to 2200 nm are presented in this paper for hydrogenated silicon (Si:H) thin films deposited by plasma enhanced chemical vapor deposition (PECVD) using the layer-by-layer (LBL) deposition technique. The films were deposited on quartz substrate by decomposition of SiH_4 *and* H_2 *gases at flow-rate of 5 sccm and 20 sccm, respectively. The substrate temperature, deposition pressure and deposition rate are 100°C, 0.8 mbar and 2.8 nm/s, respectively. The as-prepared films were annealed in nitrogen for one hour at annealing temperatures of 400°C, 600°C, 800°C and 1000°C. The as-prepared film thickness of 301 nm decreased to 260 nm when samples were annealed at 1000°C. The refractive indices (~ 3.0 to 3.4) of annealed films were determined from the interference fringes of transmission spectrum following Manifacier and Davies methods. The electronic transition from valence band to conduction band in these films are characterized from the optical energy gap;* E_G *(~1.64 to 2.41 eV), the dispersion energy;* E_d *(~26.4 to 34.0 eV) and the oscillator strength;* E_o *(~2.8 to 3.2 eV). It is interesting to note that* E_G *is lowest for the films annealed at temperature of 600°C which has the lowest hydrogen content,* C_H *in the film. Evidence of the presence of nanocrystallites formed in amorphous matrix is also observed for the films annealed at temperatures above 600°C.*

Keywords: layer-by-layer; optical constants; Si:H film

ABSTRAK

Pemalar optik diterbitkan daripada spektrum pancaran (T) dan pantulan (R) optik dalam julat panjang gelombang 220 nm ke 2200 nm dibentangkan dalam kertas ini. Filem nipis silikon berhidrogen (Si:H) dimendapkan dengan sistem pemendapan wap kimia secara peningkatan plasma (PECVD) menggunakan teknik lapisan demi lapisan (LBL). Filem nipis dimendapkan di atas substrak kuartz daripada pemisahan komposisi gas SiH_4 *dan* H_2 *pada kadar aliran 5 sccm dan 20 sccm masing-masing. Suhu substrak, tekanan pemendapan dan kadar pemendapan adalah 100°C, 0.8 mbar dan 2.8 nm/s masing-masing. Filem asal yang terhasil dipanaskan dalam suhu 400°C, 600°C, 800°C dan 1000°C dalam aliran nitrogen selama satu jam. Ketebalan filem asal berkurang daripada 301 nm ke 260 nm apabila filem nipis dipanaskan sehingga 1000°C. Indeks biasan (~ 3.0 to 3.4) bagi filem nipis yang telah dipanaskan ditentukan daripada pingiran interferen spektrum pancaran berdasarkan kaedah* Manifacier and Davies. *Transisi elektronik dari jalur valen ke jalur konduksi dalam filem nipis ini dicirikan daripada jurang tenaga optik;* E_G *(~1.64 to 2.41 eV), tenaga sebaran;* E_d *(~26.4 to 34.0 eV) and kekuatan pengayun;* E_o *(~2.8 to 3.2 eV). Adalah sangat penting untuk menunjukan bahawa* E_G *paling rendah pada filem nipis yang telah dipanaskan pada suhu 600°C yang mempunyai kandungan hidrogen paling rendah. Bukti kewujudan nanohablur terbentuk di dalam amorfus matrik boleh diperhatikan dalam filem nipis yang dipanaskan pada suhu lebih 600°C.*

Kata kunci: Filem nipis Si:H; lapisan-demi-lapisan; pemalar optik

INTRODUCTION

Knowledge on the dependence of optical constants of a material on the wavelength is very essential in obtaining fundamental information on its optical behavior in relation to its electronic transition. This is important in the application of the material in devices. Usually, the interference fringes present in the optical transmission and reflection spectra are employed to determine the thickness and refractive index of the film (Cody 1981; Kubinyi et al. 1996; Swanepoel 1983, 1984; Torres 1996). From these data, the dispersion of the refractive index, extinction coefficient, absorption coefficient with wavelength can be determined using specific numerical techniques (Cody 1981; Kubinyi et al. 1996; Swanepoel 1983 & 1984; Torres 1996). The aim of this work is to study the optical parameters and electronic transition properties of hydrogenated silicon (Si:H) thin films, as-prepared and annealed at different temperatures using established empirical relations.

METHODOLOGY

The hydrogenated silicon (Si:H) thin films in this work were deposited on quartz substrate using a home-built rf PECVD (13.56 MHz) system from the discharge of SiH_4 and H_2 gas mixture using the layer-by-layer technique. The details of the deposition system have been described elsewhere (Goh & Rahman 2006). The deposition pressure and deposition temperature were maintained at 0.8 mbar and 100°C, respectively. The RF power was fixed at 20 W which corresponded to a power density of 700 mW/cm^2. The SiH_4 and H_2 flow-rates were fixed at 5 sccm and 20 sccm, respectively producing a H_2 to SiH_4 flow-rate ratio of 4. In this study, a set of films consisting of the as-deposited film and films annealed at temperatures of 400°C, 600°C, 800°C and 1000°C were studied. The films were annealed for one hour at these temperatures using a conventional furnace (Carbolyte CFM 12/1) in ambient nitrogen gas flow.

The optical transmission and reflectance spectra were obtained using a JASCO V570 ultra-violet visible near-infrared (UV-VIS-NIR) spectrophotometer and from these spectra, the optical parameters were determined using various optical calculations. These techniques were performed on the films after every annealing process to study the effects of annealing temperature on the optical constants and its electronic transition properties.

RESULTS AND DISCUSSION

Figure 1 illustrates the optical transmittance spectra of the as-prepared film and the films annealed at 400°C, 600°C, 800°C and 1000°C. The transmission interference peak intensities in the short wavelength region decreased with increase in annealing temperature up to 600°C and increased again with further increase in annealing temperature up to 1000°C. The absorption edge in the spectral region close to the UV region red-shifted with increase in annealing temperature up to 600°C and blue-shifted towards the the UV region with further increase in annealing temperature to 1000°C. Figure 2 shows the optical reflectance spectra for the as-prepared film and film annealed at different annealing temperatures.

The interference fringes for the as-prepared film ended at ~432 nm and the smooth feature in the ultra-violet (UV) region indicate the amorphous nature of the film (Roy et al. 2008). When annealed at 400°C and 600°C, the interference fringes shifted towards longer wavelength of 452 nm and 458 nm, respectively and an increase in the amplitude of the fringes was observed. The interference fringes shifted to shorter wavelengths of 416 nm and 412 nm when the films were annealed at 800°C and 1000°C respectively and the amplitude of the interference fringes were also significantly reduced. The blue-shift of the interference fringes and absorption edges of the reflectance and transmission spectra for the films annealed at high annealing temperatures suggested a phase transition from amorphous to possibly nano-crystalline phase of the film structure. The appearance of two clear peaks at 274 nm and 360 nm in the ultra-violet region for the films annealed at temperatures of 800°C and 1000°C is a clear indication of this phase transition (Roy et al. 2008).

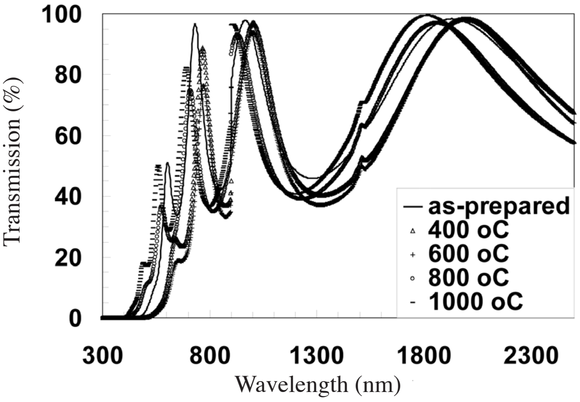

FIGURE 1. Optical transmission spectra of the as-prepared Si-H film and the films annealed at different annealing temperatures

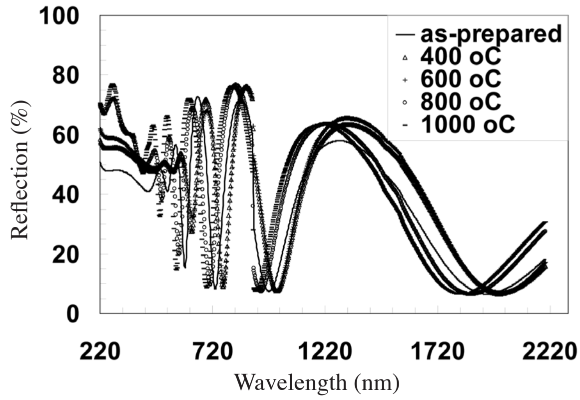

FIGURE 2. Optical reflection spectra of the as-prepared Si-H film and the films annealed at different annealing temperatures

The film thickness, *d*, refractive index, *n* and the optical energy gap; E_G, determined from optical transmission and reflection spectra are plotted against annealing temperature as shown in Figure 3. The *d* was determined from the interference fringes of transmission and reflection spectrum using the Davies method (Davies et al. 1987). The *n* was determined from the interference fringes of the transmission and reflection spectra using the Manifacier and El-Naggar Methods, respectively (Manifacier et al. 1976; El-Naggar et al. 2009). The two methods employed for determining the optical constants produced n values with similar dependence on the annealing temperature. The film thickness, however appeared to be thinner when determined using the reflectance spectra of the films. This maybe contributed by dispersion of light at uneven film surfaces. The observed decrease in *d* with increase in annealing temperature can be due to evolution of hydrogen from the film structure. The *n* increased from 3.05 for the as-prepared film to 3.42 for the film annealed at 600°C.

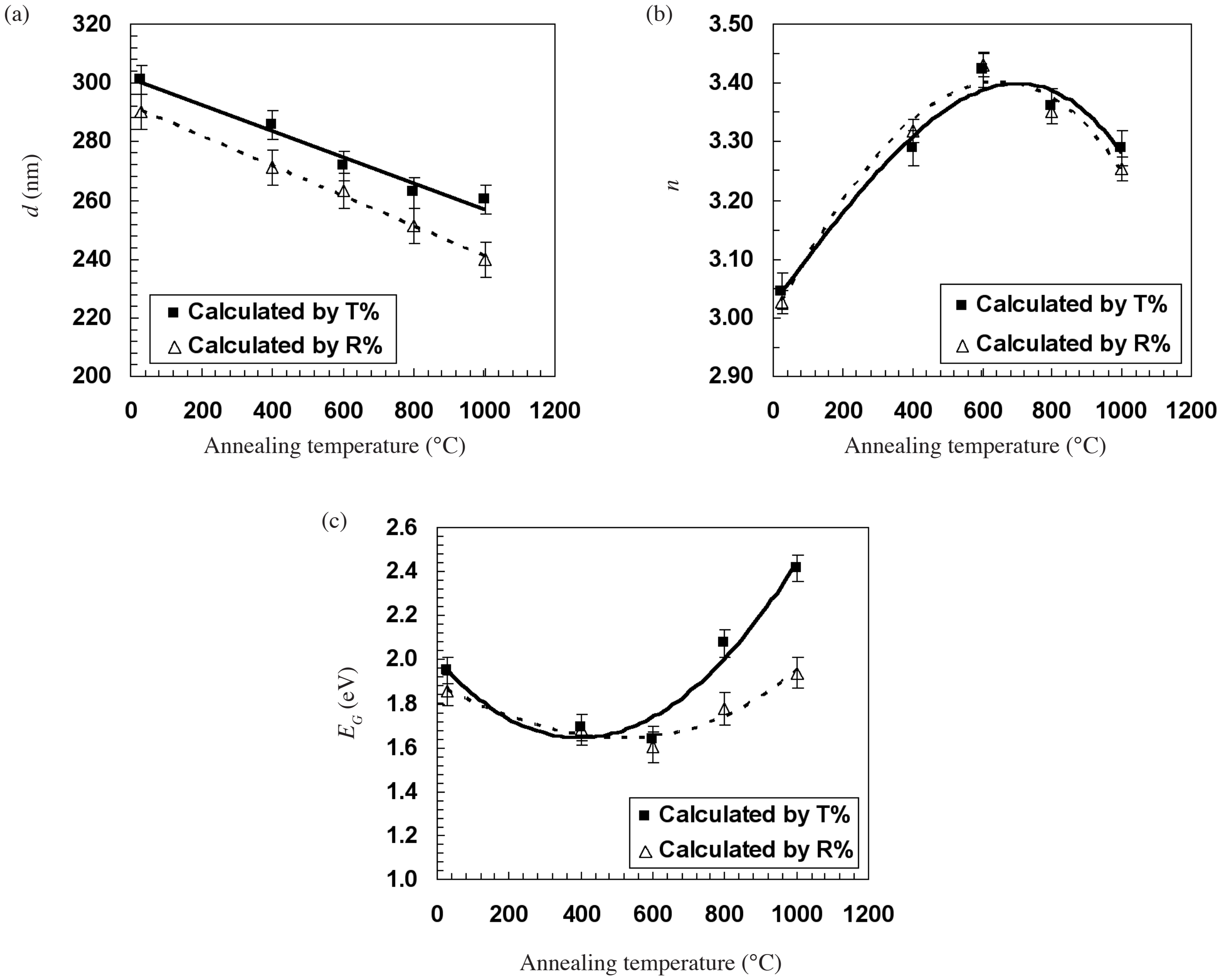

FIGURE 3. Variations of (a), d (b) n and (c) E_G determined from optical transmission and reflection spectra, with annealing temperature

Then, n decreased to 3.29 with further increase in annealing temperature up to 1000°C. The E_G was calculated using the Tauc relation (Tauc 1974)$(\alpha h\nu) = B(h\nu - E_G)^2$, where α and B are the absorption coefficient and the slope of the plot respectively. The E_G decreased from 1.95 eV for the as-prepared film to 1.64 eV for the film annealed at annealing temperature of 600°C and increased to 2.42 eV with further increase in annealing temperature up to 1000°C. The annealed films showed large optical energy gap at high annealing temperatures above 600°C. Increase in the annealing temperature beyond 600°C induced phase transition from the amorphous to nano-crystalline phase thus widening the optical band gap.

The refractive index data obtained from optical data was fitted to the Wemple and Di Domenico relation (Wemple & Didomenico 1971): $n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\nu)^2}$, where E_o is the single-oscillator energy and E_d is the dispersion energy representing a measure of the strength of inter-band optical transitions. The variation of E_d and E_o against annealing temperature is shown in Figure 4. The plots of E_d and E_o obtained from transmittance and reflectance versus annealing temperature showed similar consistent trends. E_d increased gradually with increase in annealing temperature up to 600°C and produced no further variation when the films were annealed at temperatures of 800°C and 1000°C. E_o, however decreased with increase in annealing temperature up to 600°C and increased rapidly with further increase in annealing temperature to 800°C. The E_o showed a slight decrease when the film was annealed at 1000°C. The changes of these two parameters actually indicated a change in the characteristics of the electronic transition from the valence state to conduction state of the annealed films. The parameter, β can be used to explain the properties of the electronic transition of the annealed films in further detail using the Bhattacharya relation (Krishna & Bhattacharya 2001): $\beta = \frac{E_d}{6E_G(n^2 - 1)}$, where n is the long wavelength limit of the refractive index. The β values were in the range of 0.22 – 0.30 which meant that the bonds in the films have ionic characteristics as mention in Ref. (Wemple 1973) and the films annealed at temperatures of 800°C and 1000°C were more ionic comparatively due to the presence of nano-crystalline structures in the films.

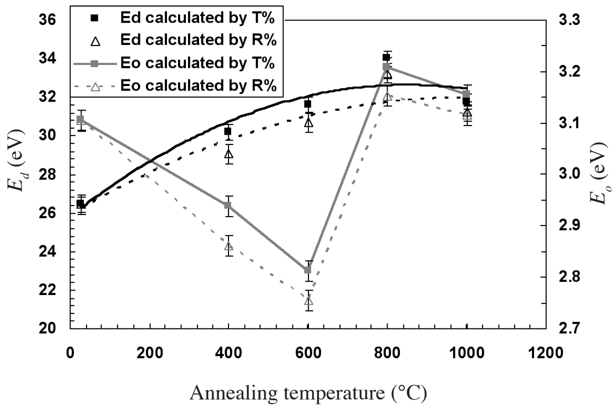

FIGURE 4. Variations of E_d and E_o with annealing temperature for Si-H films deposited by LBL deposition technique

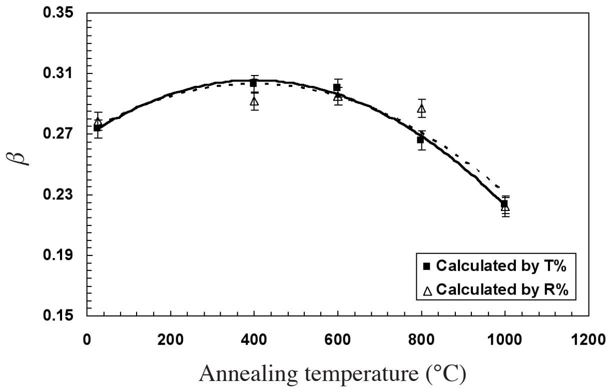

FIGURE 5. Variations of β with annealing temperature for Si-H films deposited by LBL deposition technique

CONCLUSION

The optical constants and electronic parameters in Si:H thin films deposited by LBL deposition technique, as-prepared and annealed at different annealing temperatures ranging from 100°C to 1000°C were calculated using various simple and effective methods using transmittance and reflectance data. The results showed that the values calculated using both transmittance and reflectance data produced similar trends with annealing temperature. Both the transmittance and reflectance derived parameters showed evidence of phase transition in the film structure from amorphous to nano-crystalline phase when annealed at temperatures above 600°C. The nano-crystalline films annealed at temperatures of 800°C and 1000°C have large optical energy gaps of 2.1 eV -2.4 eV and were also more ordered compared to the amorphous films.

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Received: 7 December 2009
Accepted: 13 July 2010