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Properties of rapidly deposited amorphous hydrogenated carbon films

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The properties of hydrogenated amorphous carbon films prepared by the rapid and low-temperature decomposition of toluene in an r.f. glow discharge have been investigated. The films are composed of a mixture of sp^2 and sp^3 bonded carbons. Measurements of the optical gap show that the optical gap decreases with an increase of the r.f. power and increases with increasing pressure. The room-temperature dielectric constant decreases with increasing pressure with a dielectric loss tangent of 1%.

1. Introduction

Hydrogenated amorphous carbon (a-C:H) films made from the decomposition of hydrocarbon gases have recently received considerable attention because of their hardness, optical transparency and chemical inertness. Various methods have been used to deposit these films, including the sputtering of carbon [1] and plasma deposition from hydrocarbon gases [2]. It is well known that interesting properties such as optical transparency depend strongly on the existence of hydrogen in these films [3, 4]. In general, with an increase of the hydrogen content of the films, the band gap of the films is found to become narrower by terminating the dangling bonds. The hydrogen, of course, affects the type of bonding present in the films. The C–H stretching mode around $3000\ \mathrm{cm}^{-1}$ is a main absorption band, as well as the C–C stretching mode around $1330\ \mathrm{cm}^{-1}$ in the hydrogenated amorphous carbon films [5].

The present study addresses a-C:H films from the viewpoint of rapid and low-temperature decomposition using toluene. Low-temperature decomposition is necessary for the application of these films in the field of microelectronics. The optical properties of these films are also of importance because of their application for use as optical elements. This paper characterizes a-C:H films prepared under a flow of toluene vapour for a couple of minutes at substrate temperatures of 30–60 °C. The optical constants of the films were determined by using a double-beam spectrometer. Data on the dielectric constant and density of these films were also obtained and are reported.

2. Experimental procedure

The a-C:H films were prepared by r.f. plasma deposition from toluene vapour. The gas was introduced and 40 W of 13.56 MHz r.f. power was used to produce a discharge. Most of the films were deposited on n-type silicon wafers; however, a few were also deposited on fused silica and stainless steel substrates.

Raman spectroscopy was performed by backscattering from the a-C:H films using an argon-ion laser operating at 514.5 nm at a power of 0.1 W. The optical constants of the films were determined in the photon energy range 0.5–4.5 eV by analysis of both the reflectance and transmittance data. A double-beam spectrometer was employed to complete measurements in the wavelength range 190–900 nm, covering the u.v. and the visible.

Only qualitative attempts were made to evaluate the properties of the films prepared by rapid and low-temperature decomposition. The surface temperatures of the substrate were changed from 30 to 60 °C depending on the r.f. power in this study. Therefore, the hydrogen content is not quantitatively evaluated in the films from the absorption spectra. Quantitative evaluation of the hydrogen content was carried out by using secondary ion mass spectroscopy (SIMS). A Talystep recorder was used to measure the film thickness.

3. Results and discussion

The morphology and structure of the deposited films were observed by SEM and Raman spectroscopy. The surface topology of the a-C:H films in this study looks like ball-like particles without any crystalline habit [6]. A columnar structure was observed in the cross-section of the films [7]. The growth rate is shown in Fig. 1. It was found that the growth rate obtained is approximately $500\ \mathrm{nm\ min}^{-1}$, and also that the thickness of the film increases with an increase of the discharge power. Fig. 2 shows a typical Raman spectrum for a film deposited on a stainless steel substrate with a discharge power of 40 W, and a gas pressure of 26 Pa. Raman spectra were essentially identical with the results for hydrogenated amorphous carbon films

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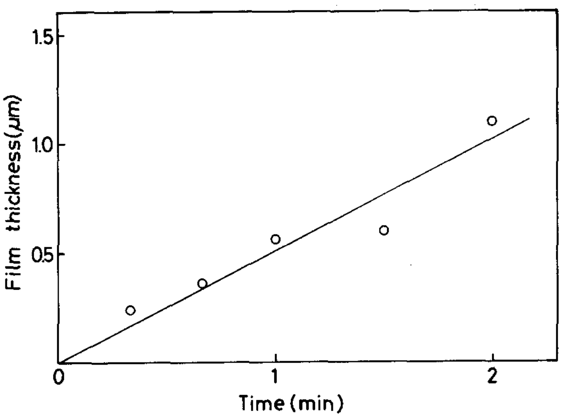

Figure 1 Relationship between the film thickness and deposition time. Substrate: Si (n-type), substrate temperature: 60 °C, gas source: toluene, r.f. power: 130 W, pressure: 45 Pa.

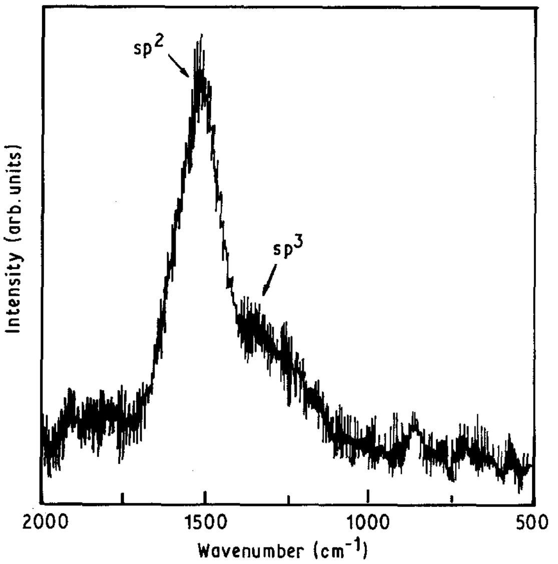

Figure 2 A typical Raman spectrum of the as-deposited films. Substrate: SUS430 (oxide), gas source: toluene, r.f. power: 40 W, pressure: 26 Pa.

[8, 9], namely a broad peak lying between 1100 and 1600 cm^{-1}. Fig. 3 shows the effect of gas pressure on the Raman spectra. By increasing the gas pressure, the peak position of the main spectra shifts to a lower wave number; however, the intensity of the peak is gradually decreased.

The optical gap is a very useful parameter for the characterization of amorphous semiconducting films such as these a-C:H films. It can be extracted from the energy dependence of the imaginary part of the dielectric constant. The relationship between (absorption × energy)$^{1/2}$ and photon energy yields a straight line except for the lowest tails. Therefore, by extrapolating the straight line to the abscissa, one can easily obtain the value of the optical gap. The optical gap obtained for these a-C:H films is shown in Fig. 4. A gradual decrease of the width of the optical gap with increasing r.f. power is observed. In general, it is well known that the content of hydrogen in the films affects the optical gap in amorphous hydrogenated carbon films. That is, the greater the hydrogen content, the higher the optical gap energy.

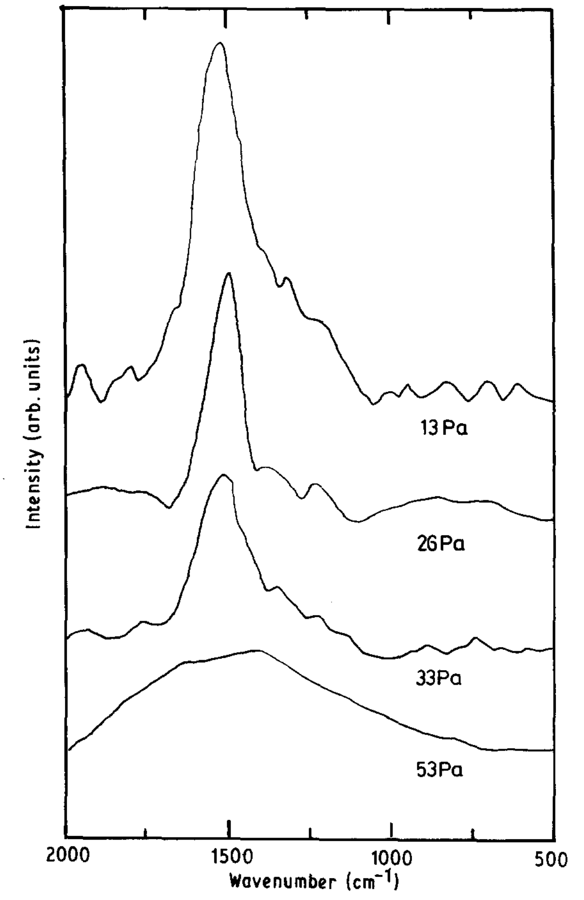

Figure 3 The change in Raman spectra with the reaction pressure. R.f. power: 40 W.

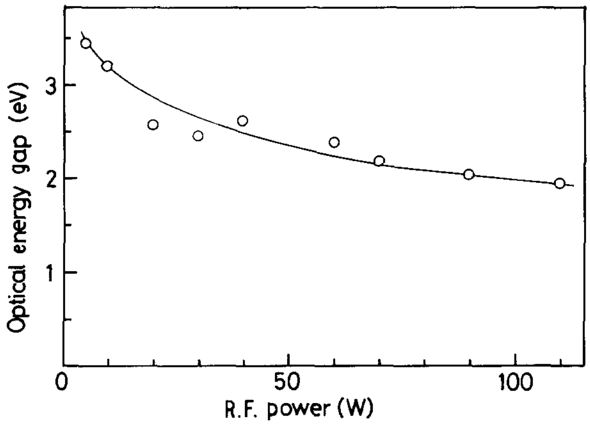

Figure 4 Relationship between the optical gap and r.f. power. Substrate: Corning 7059, pressure: 26 Pa.

The SIMS results show a decrease of hydrogen content with increasing r.f. power as shown in Fig. 5. The hydrogen content in the amorphous carbon films depends strongly on the bias voltage [10]. It is well known that the bias voltage is proportional to the r.f. power. Therefore, with increasing bias voltage the hydrogen content decreases and so does the optical gap.

Many hydrogen atoms may be included in the films during the deposition process because of non-completion of the gas discharge reactions. The influence of gas pressure on the optical gap is shown in Fig. 6. With increasing gas pressure the optical gap increases and so does the hydrogen content. These data on the

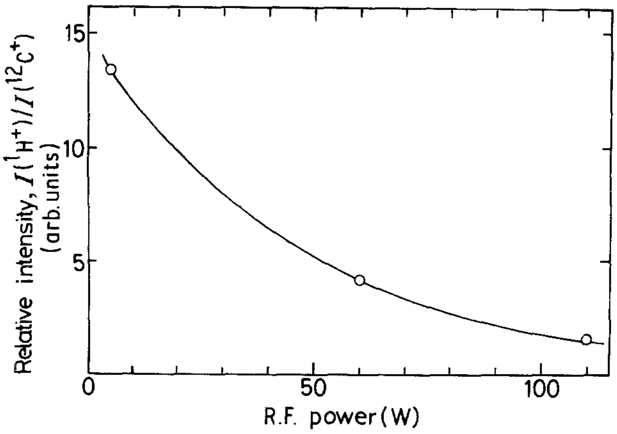

Figure 5 Relationship between the relative intensity of hydrogen to carbon and r.f. power. Gas source: toluene, pressure: 26 Pa.

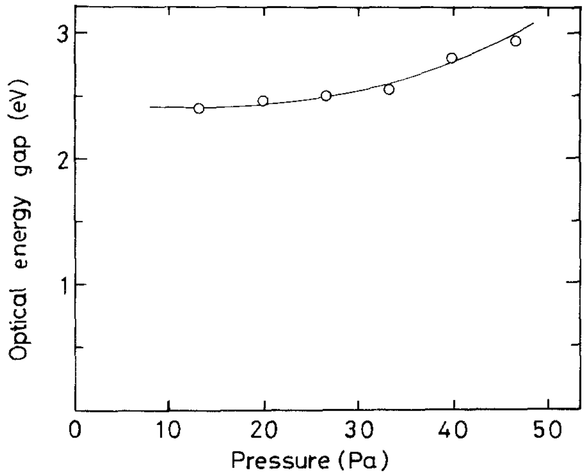

Figure 6 Variation of the optical gap with gas pressure. Substrate: Corning 7059, r.f. power: 20 W, gas source: toluene.

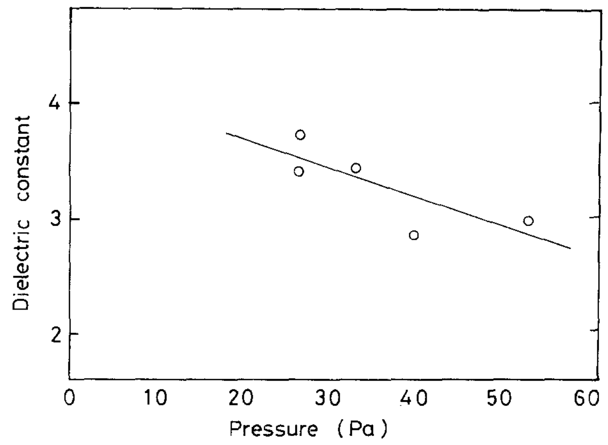

Figure 7 Variation of the dielectric constant with gas pressure. R.f. power: 140 W.

optical gap strongly support the fact that dangling bonds in the films have been terminated by hydrogen, and this results in the increase of optical gap. The status of excess hydrogen may be unstable, therefore additional treatments such as heat treatment may cause a decrease of the hydrogen content. On increasing the annealing temperature in a vacuum, a rapid decrease of the hydrogen content above 300 °C is observed.

As is well known, a low dielectric constant of the substrates for use in high-frequency circuits is an essential factor. However, only a few reports on the dielectric constant of a-C:H films are available in the literature. Therefore the dielectric constant of the films was measured at 1 MHz at room temperature. The results are shown in Fig. 7. The dielectric constant of the films decreased from 3.8 to 2.8 with increasing gas pressure. The density of the films also decreased from 1.6 to 1.1 $g\,cm^{-3}$ with increase of the pressure.

4. Conclusions

Rapid and low-temperature decomposition for the formation of a-C:H films was performed by the r.f. glow-discharge decomposition of toluene vapour. The nature of the as-deposited films is essentially a mixture of sp^2 and sp^3 bonded carbons. The optical gap of the films shows that a significant dependency on the discharge power arises from the presence of hydrogen in the films. The dielectric constant is decreased from 3.8 to 2.8 with increasing gas pressure. The dielectric loss tangent is 1% at 1 MHz.

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