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Optical Properties of Hydrogenated Amorphous Carbon Films Grown from Methane Plasma

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OPTICAL PROPERTIES OF HYDROGENATED AMORPHOUS CARBON FILMS GROWN

FROM METHANE PLASMA

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SUMMARY

We have used a 30 kHz ac glow discharge formed from methane gas to grow carbon films on InP substrates. Both the growth rate, and the relative Ar ion sputtering rate at 3 keV varied monotonically with deposition power. The Ar ion etching rate of the films decreased with deposition power. Results from the ^{15}N nuclear reaction profile experiments indicated a slight drop in the hydrogen concentration as more energy was dissipated in the ac discharge. Values for the index of refraction and extinction coefficient ranged from 1.721 to 1.910 and 0 to -0.188, respectively. Optical bandgaps as high as 2.34 eV were determined.

INTRODUCTION

Carbon films can be formed on different substrates by ion-beam deposition (ref. 1), ion-beam sputtering (refs. 2 to 6) and plasma deposition of gaseous hydrocarbons (refs. 4 to 7). The resulting films are generally hard, semi-transparent and they exhibit high electrical resistance. Their properties may therefore be amenable to semiconductor processing. The optical and electrical properties of films grown on Si have been reported recently (refs. 3, 6, and 7).

In this paper, we present results on the effect of plasma parameters on carbon film growth. Single crystal InP wafers are used as substrates. Data on the complex index of refraction and hydrogen concentration are also reported.

EXPERIMENTAL

A planar plasma reactor operating at 30 kHz was used for the growth experiments. The power was capacitively coupled to the upper electrode, and the bottom electrode and chamber wall were grounded. The chamber pressure was regulated by the input gas flow rate and pumping speed.

Initially, the InP wafers were cleaned successively in acetone and ethanol baths, and rinsed in deionized water. The samples were then placed on the grounded anode; the chamber pressure was typically 20 mTorr. Methane gas (99.97 percent) was used to flush the system three times prior to each run. Amorphous carbon films were formed on the InP substrates from the ac glow dis-

charge. The deposition power, P, and flow rate, f, settings were varied from 25 to 390 W and 30 to 90 sccm, respectively. The initial substrate temperature was ~23 °C, and it increased a few degrees during deposition. A mass flow controller stabilized the flow rate during the growth experiments. The pressure, p, in mTorr varies linearly with flow rate, and the relationship is: p = 3.5f + 70.

Analyses of film composition were obtained using a PHI AES/ESCA system interfaced with a PHI Multiple Technique Analytical Computer System. Depth profiles were performed by sputtering with 3 keV Ar ions. The beam current used was 25 mA.

The nuclear reaction profile experiments were performed at the SUNY-Albany accelerator facility. In this technique, a ^{15}N beam interacts with the hydrogen in the carbon films. Since this reaction is resonant at 6.385 MeV (laboratory frame of reference), the intensity of the 4.43 MeV γ-rays emitted provides the hydrogen concentration information (ref. 9).

The film thickness, refractive index and extinction coefficient were determined using a semiautomatic Gaertner L119X research ellipsometer in the rotating analyzer mode. A He-Ne laser and a 100 W Hg arc lamp were used. Data acquisition and analysis were done by an on-line computer. A least squares fit to a three phase model (ambient, film, substrate) was performed. A multiple wavelengths and angles of incidence fitting program (ref. 10) was used. All experimental points obtained on each sample were used in each least squares fit.

RESULTS AND DISCUSSIONS

AES compositional analyses and profiles showed only carbon was present in each film. Up to 4 percent of oxygen were evident at the carbon-InP interface.

Film thicknesses, δ, were obtained using ellipsometry. Figure 1 illustrates the typical dependence of growth rate on deposition power. The samples are carbon films grown on InP using a methane flow rate of 70 sccm. This growth rate increases from ~5 to ~27 nm/min as the power increases from 25 to 300 W.

The relative Ar ion sputtering rate, G, at each power was defined by the relation G = tp/td, where tp is the AES profiling time for the carbon film and td is the deposition time. Figure 2 shows that G (for 3 keV Ar ions) varies monotonically with deposition power/pressure ratio (or "average" energy per particle) at a fixed pressure. For increasing powers (fixed pressure), the relative sputtering rate increases and appears to saturate at higher powers. We note for powers greater than 75 W that G increases with pressure (fixed power).

The Ar ion etching rate, ER, of the carbon films is defined as ER = δ/tp. A plot of ER (for 3 keV Ar ions) versus deposition power is shown in Fig. 3. An inverse relationship between ER and P is observed, ER drops from ~8 to ~5 nm/min when P is increased from 25 to 300 W. This suggests that films grown at higher powers are harder and/or denser than those grown at lower powers. The ^{15}N nuclear reaction analyses data in Fig. 3 show that the hydrogen concentration in the carbon film decreases slightly with increasing

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power. The hydrogen concentrations are in the 7.2 to $7.7 \times 10^{22}/cm^3$ range. It appears that a decrease in hydrogen concentration is accompanied by an increase in film density and/or C-C bondings.

Indices of refraction, n, and extinction coefficients, k, were determined by ellipsometry. The n and k results in the wavelength range 632.8 to 365 nm are summarized in Tables I and II. The samples were carbon films grown on InP substrates using a constant flow rate, and deposition powers from 50 to 300 W. Except for the highest power (300 W), the refractive index decreases systematically with increasing wavelength. Note that all values of n lie within a band $\Delta n \sim 0.2$. The absolute value of the extinction coefficient decreases with increasing wavelength. For example, at 300 W, |k| changes from ~0.19 (365 nm) to ~0.04 (577 nm). In addition, |k| increases with P (fixed wavelength).

The equation $\alpha = 4\pi k/\lambda$ was used to compute the absorption coefficient, α, as a function of wavelength, λ. In order to evaluate the optical bandgap, Eg, we referred to the relation $(\alpha h\nu) = A(h\nu - Eg)^2$ which describes the interband optical absorption in a noncrystalline solid (ref. 11). The photon energy is $h\nu$ and A is a constant. Values for the bandgap were deduced from plots of $\alpha h\nu$ as a function of $h\nu$. The results are shown in Fig. 4.

At fixed wavelength, the refractive index increases with power. This fact by itself can be explained by assuming a change in the void fraction as a function of power and using the effective medium approximation (EMA) (ref. 8). However, results on the optical bandgap contradict this explanation. Changes in the void fraction will change the fitting constant A, but not the value of Eg. It seems that we have changes in the properties of the carbon film, with or without a possible void fraction variation. Attempts to fit an EMA model to carbon film data proved to be unsuccessful (ref. 12). Therefore, we could not estimate the separate contributions of voids and different types of carbon.

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TABLE I. - INDEX OF REFRACTION (n) OF CARBON FILMS
FOR DIFFERENT WAVELENGTHS (λ) AND POWERS (p)

$\lambda(\text{Å})$ / P(W)	3650	4047	4358	5461	5770	6328
50	1.801	1.790	1.780	1.734	-----	1.721
100	1.846	1.801	1.798	1.743	1.743	1.727
150	1.864	1.818	1.815	1.764	1.760	1.748
200	1.842	1.838	1.835	1.783	1.787	1.765
300	1.899	1.906	1.910	1.888	1.849	1.836

TABLE II. - EXTINCTION COEFFICIENT (k) OF CARBON FILMS
AND POWER AS A FUNCTION OF WAVELENGTH AND POWER

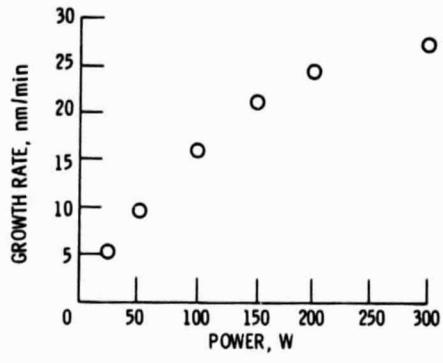| $\lambda(\text{Å})$ / P(W)	3650	4047	4358	5461	5770	6328
50	-0.072	-0.044	-0.023	0	0	0
100	-.088	-.051	-.032	0	0	0
150	-.093	-.063	-.042	0.007	-0.002	0
200	-.116	-.080	-.054	-.014	-.006	0
300	-.188	-.144	-.107	-.038	-.036	0

Fig. 1. - Growth rate of hydrogenated car-
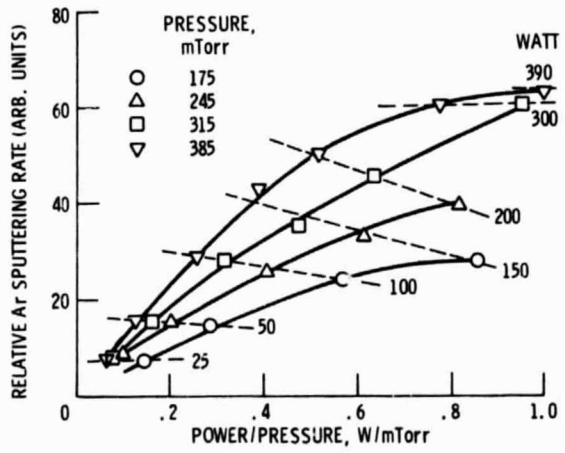bon on n - InP as a function of deposition
power.

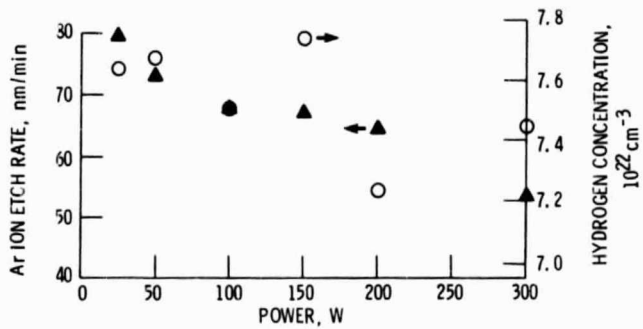Fig. 2. - Relative Ar sputtering rate as a function of
power/pressure.

Fig. 3. - Ar ion etching rate (▲) and hydrogen concen-
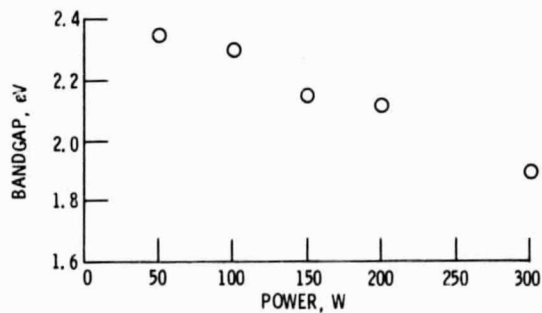tration (O) as a function of deposition power for carbon
film grown on n - InP.

Fig. 4. - Optical bandgap as a function of deposition
power for carbon film grown on n - InP.

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15. Supplementary Notes

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