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# Hydrogenated amorphous carbon films deposited by low-frequency plasma chemical vapor deposition at room temperature

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Hydrogenated amorphous carbon ( $a$ -C:H) films were prepared at room temperature by low-frequency (50-Hz) plasma chemical vapor deposition using  $\text{CH}_4$  and  $\text{H}_2$ . The  $a$ -C:H films were transparent, highly resistive, and very uniform. Infrared absorption measurements, as well as Raman spectroscopy, indicated that the C bonding in the  $a$ -C:H films was predominantly  $sp^3$ . Moreover, the optical band gap of the  $a$ -C:H films was measured.

Hydrogenated amorphous carbon ( $a$ -C:H) films show large thermal conductivity, chemical inertness, high electrical resistivity and breakdown field, and optical transparency, all of which are suitable for the coating material in microelectronics as well as in mechanical applications. A number of reports have been published on the preparation of  $a$ -C:H films by various methods.<sup>1-4</sup> The low-temperature formation of such an  $a$ -C:H film is required for microelectronics application.

This communication reports the deposition of high-quality  $a$ -C:H films, with the majority of C in the  $sp^3$  bonding configuration, on Si and glass substrates at room temperature by very-low-frequency (50 Hz) plasma chemical vapor deposition (CVD) using  $\text{CH}_4$  and  $\text{H}_2$ . This method has been used to successfully deposit high-quality SiN films at room temperature from  $\text{SiH}_4$  and  $\text{N}_2$ .<sup>5</sup> Note that there is no need for frequency conversion for the 50-Hz plasma, which results in an inexpensive plasma CVD apparatus with less overall power consumption.

$a$ -C:H films were prepared using the experimental setup shown in Fig. 1. The vacuum chamber was made of stainless steel with a glass bell jar and was pumped by a turbomolecular pump. The background pressure was  $5 \times 10^{-7}$  Torr. The

electrodes were made of 12-cm-diam stainless steel with a 2-cm gap between the two electrodes. Silicon and glass substrates on which the  $a$ -C:H deposition occurred were placed on the lower electrode. No substrate heating was employed throughout the entire course of the work.

The gases used in the experiment were  $\text{CH}_4$  (99.99%) and  $\text{H}_2$  (99.99999%). These gases were introduced in the chamber at a rate of 4–7 sccm and 300–350 sccm, respectively. At a total pressure of 1.0–1.5 Torr, a low-frequency plasma of 50 Hz was excited between the electrodes to deposit  $a$ -C:H films on substrates. This was done by applying 400 V<sub>rms</sub> (50 Hz) to the upper electrode while the lower electrode is grounded. The current was 3–8 mA ( $2.5$ – $7.1 \mu\text{A}/\text{cm}^2$ ).

Resistivity as well as the breakdown electric field were measured after the deposition. The refractive index was measured by ellipsometry. Moreover, the optical band gap was measured. Infrared absorption measurement and Raman spectroscopy were used to investigate the bonding nature of the deposited  $a$ -C:H films.

The grown films were highly transparent and showed very uniform interference color. The interference color was extremely uniform over a 4-in. Si wafer except for the region of 5 mm from the peripheral, reflecting the uniform and sta-

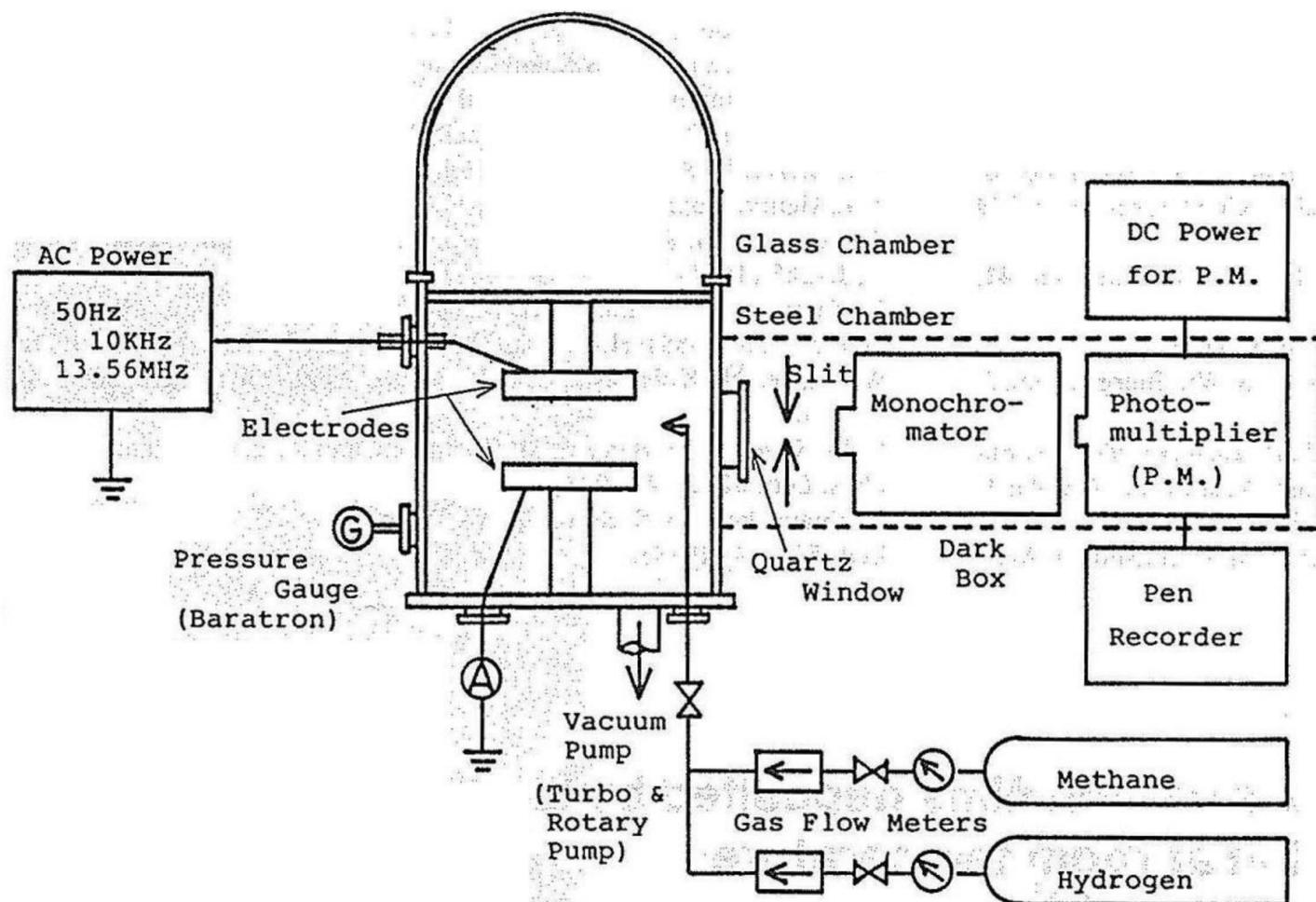


FIG. 1. Schematic diagram of the plasma CVD apparatus used in the present work.

ble nature of the 50-Hz plasma. The deposition rate of  $a$ -C:H films under the condition specified above was 60 Å/h.

Major electrical and optical properties of the present  $a$ -C:H films were summarized in Table I, where resistivity, breakdown electric field, optical band gap, refractive index, film color, and surface morphology were listed. A high resistivity of more than  $10^{14}$  Ω cm with high breakdown field is particularly suitable for interlayer insulation for microelectronics. Adhesion to Si wafers was quite good and no cracking was observed after annealing of 600 °C for 10 min.

Figure 2 shows the infrared absorption spectrum of the grown film for the C-H stretching mode region. The spectrum can clearly be decomposed to four Gaussian components, as shown in Fig. 2. All Gaussian peaks are related to the  $sp^3$ -coordinated C[C( $sp^3$ )-H] which lies in the region from 2850 to 2960 according to Dischler *et al.*<sup>6</sup> No absorption related to  $sp^1$  bond (3300–3310  $cm^{-1}$ ) was seen in the spectra. Since the main peak of 2950  $cm^{-1}$  was broad, it is not clear whether C( $sp^2$ )-H related absorption (3010–3095  $cm^{-1}$ ) is totally absent, but the magnitude must be very small compared to the C( $sp^3$ )-H related absorption. It may be concluded from Fig. 2 that the type of bonding at C adjacent to H is predominantly  $sp^3$ .

Figure 3 shows the Raman spectrum of the grown

$a$ -C:H film using Ar<sup>+</sup> laser (514.5 nm) excitation. As can be seen in Fig. 3, a peak at around 1550  $cm^{-1}$  with a shoulder around 1400  $cm^{-1}$  was observed from all the samples measured by Raman spectroscopy, which is very similar to what was observed for the  $sp^3$ -rich  $a$ -C:H<sup>2</sup>. The peak at 1550  $cm^{-1}$  arises from the C  $sp^2$  bonds whereas it arises at the shoulder from C  $sp^3$  bonds. Taking into account that the Raman efficiency for the  $sp^3$  bonds is only 2% of that of  $sp^2$  bonds,<sup>7</sup> Fig. 3 also indicates that the  $sp^3$  bonding configuration dominates in the present samples. It should be noted that a broad peak at around 1300–1400  $cm^{-1}$ , which is caused by the microcrystals in the sample, is often observed in graphite samples.<sup>8</sup> This is not the case for the present sample since reflection

TABLE I. Properties of the  $a$ -C:H films prepared by 50-Hz plasma CVD.

	$a$ -C:H film	Natural diamond
Resistivity (Ω cm)	$> 10^{14}$	$10^{13}$ – $10^{16}$
Breakdown field (V/cm)	$> 10^6$	
Optical band gap (eV)	4	5–6
Refractive index	2.4	2.4
Color	transparent	transparent
Surface morphology	mirrorlike	

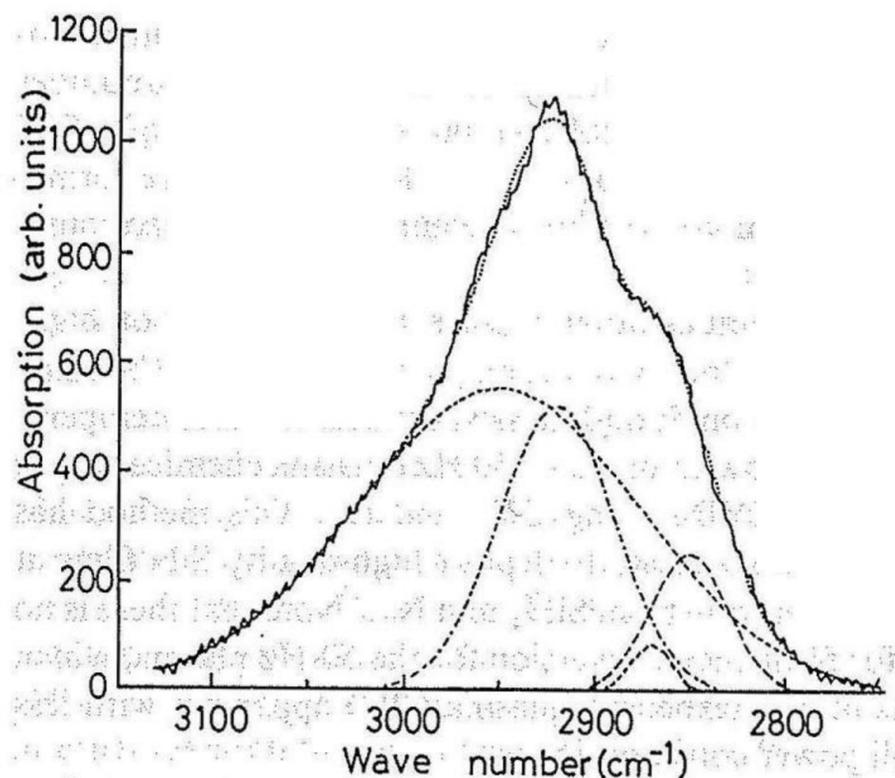


FIG. 2. Infrared absorption spectrum of  $a$ -C:H film in the region where the stretching mode of C-H appears. The spectra can be decomposed to four Gaussian curves, all of which are associated with the  $sp^3$  bonding configuration of the adjacent C.

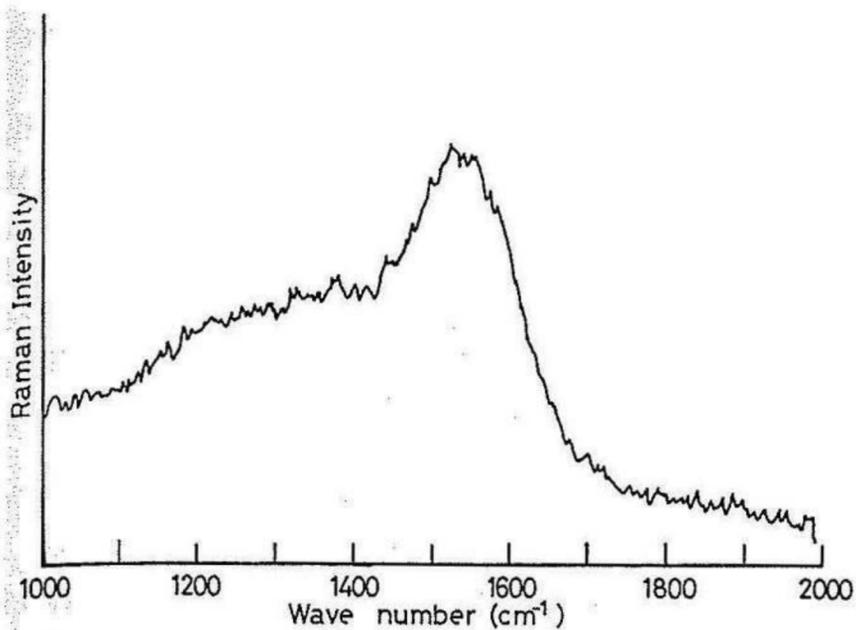


FIG. 3. Raman spectrum of  $a$ -C:H film. The peak at around  $1550\text{ cm}^{-1}$  is attributed to the peak related to the  $sp^2$ -coordinated C whereas the shoulder around  $1400\text{ cm}^{-1}$  to  $sp^3$ -bonded C. Note that Raman efficiency is only 2% for  $sp^3$  bonds and thus the spectrum indicates the bonding in the film being predominately  $sp^3$ .

high-energy electron diffraction patterns of the present samples show a complete amorphous nature with no indication of microcrystals.

The reason for the successful deposition of high-quality  $a$ -C:H films by the present method at room temperature can probably be attributed to the nature of the plasma excited by the present method. Recent measurements of the light emission spectra of the 50-Hz plasma of  $\text{SiH}_4$  and  $\text{N}_2$  revealed that the electron energy in the 50-Hz plasma was higher than that of plasma excited by 13.56 MHz.<sup>9</sup> The high-energy electrons allow the further dissociation of the source molecules,

which is probably the reason why high-quality films can be deposited by the present low-frequency plasma CVD even at room temperature.

In summary, transparent and highly uniform  $a$ -C:H films were deposited on Si as well as on glass substrates at room temperature by plasma CVD with a very low frequency of 50 Hz using  $\text{CH}_4$  and  $\text{H}_2$ . The deposited films were highly resistive ( $> 10^{14}\ \Omega\text{ cm}$ ) with high breakdown field strength ( $> 10^6\ \text{V/cm}$ ). Moreover, the optical band gap of the film was 4 eV. Infrared absorption as well as Raman spectroscopy showed that the film predominantly consisted of  $sp^3$ -bonded C.

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