Instructions for use

Title
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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 CH₄ and H₂. 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 sp³. 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. 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 sp³ bonding configuration, on Si and glass substrates at room temperature by very-low-frequency (50 Hz) plasma chemical vapor deposition (CVD) using CH₄ and H₂. This method has been used to successfully deposit high-quality SiN films at room temperature from SiH₄ and N₂. 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 × 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 CH₄ (99.9999%) and H₂ (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 rms (50 Hz) to the upper electrode while the lower electrode is grounded. The current was 3–8 mA (2.5–7.1 μA/cm²).

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-
The sp3-poordinated C-[C(sp3)-H] which lies in the region components, as shown in Fig. 2. All Gaussian peaks are related to bonding configuration dominates.

Figure 3 shows the Raman spectrum of the grown 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 sp3 bonding configuration of the adjacent C.

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

<table>
<thead>
<tr>
<th>Property</th>
<th>a-C:H film</th>
<th>Natural diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω cm)</td>
<td>&gt;10¹⁴</td>
<td>10¹³-10¹⁶</td>
</tr>
<tr>
<td>Breakdown field (V/cm)</td>
<td>&gt;10⁴</td>
<td>4-6</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>4-6</td>
<td>4-6</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Color</td>
<td>transparent</td>
<td>transparent</td>
</tr>
<tr>
<td>Surface morphology</td>
<td>mirrorlike</td>
<td></td>
</tr>
</tbody>
</table>

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 sp3 bonding configuration of the adjacent C.

α-C:H film using Ar+ 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 sp³-rich α-C:H². The peak at 1550 cm⁻¹ arises from the C sp² bonds whereas it arises at the shoulder from C sp³ bonds. Taking into account that the Raman efficiency for the sp³ bonds is only 2% of that of sp² bonds, Fig. 3 also indicates that the sp² 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. This is not the case for the present sample since reflection
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 SiH₄ and N₂ revealed that the electron energy in the 50-Hz plasma was higher than that of plasma excited by 13.56 MHz.⁹ 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 CH₄ and H₂. The deposited films were highly resistive (> 10¹⁴ Ω cm) with high breakdown field strength (> 10⁶ 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 sp³-bonded C.

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