Silicon films deposited on flexible substrate by hot-wire chemical-vapor deposition

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1. Introduction

Microcrystalline silicon (μc-Si) is a two-phase material in which crystalline regions are embedded in an amorphous matrix. Because the optical absorption of μc-Si is superior to that of crystalline silicon, μc-Si film has received considerable attention in recent years. In addition, in contrast to amorphous silicon, μc-Si has stable transport properties that are not influenced by light degradation [1]. Hot-wire chemical-vapor deposition (HW-CVD) technology has been considered favorably as an alternative deposition method for hydrogenated amorphous silicon [2,3] and μc-Si [4] because it can achieve higher deposition rates [3] and improved film stability [5].

Cyclic olefin copolymer (COC) was used as flexible substrate in this study. A COC substrate is an amorphous engineering thermoplastic, used in many optical and electrical applications [6,7] because of its high optical transparency, low dispersion rate, and low water-vapor transmission rate (WVTR). The WVTR of different polymer substrates are shown in Fig. 1. Four types of polymer material were compared: polycarbonate (PC) and poly(ethylene terephthalate) (PET) substrates, and COC and annealed-COC films.

The WVTR of annealed-COC films was superior to that of unannealed COC because the dipole moments of the polymer chain in the sample tended to rearrange themselves to the preferred orientation and because molecular well-packing phenomena occurred after the thermal treatment. However, the surface was smooth after annealing, with the surface roughness reaching 1.31 nm [7]. The WVTR of the pure PC and PET substrates were extremely high because of their higher water absorption [8]. The lower WVTR of the flexible substrate could avert postoxidation of the silicon film when the silicon film was used to manufacture an electronic device. Inorganic films, such as SiN x [9], SiO 2 [10], and Al 2 O 3 [11], were deposited on flexible substrate as a barrier layer to reduce the WVTR and oxygen transmission rate (OTR). The WVTR and OTR for a flexible electronic device were kept as low as possible to avoid postoxidation.

In this study, a series of silicon films was deposited on a COC surface with different hydrogen-dilution ratios by using HW-CVD. The crystallinity, surface roughness, and optical-absorption properties of silicon films with different hydrogen-dilution ratios are discussed in this article.

2. Experiments

COC pellets were melted at 230 °C by using a hot-press machine. After the hot-press process, the COC films were annealed at 210 °C for 2 h in a vacuum environment. The silicon films were deposited...
on the COC substrate by using HW-CVD at a low-substrate temperature of 60 °C. Different ratios of silane (SiH₄) gas and hydrogen (H₂) were used during the deposition. The different hydrogen-dilution ratios (Dₜₜ) were defined as $D_{\text{H}} = \frac{[H_2]}{[\text{SiH}_4 + H_2]}$ in this study. A tungsten filament was employed as the heating source and was heated to 1650 °C. The distance from the heating source to the sample substrate was 5 cm. The crystallinity of the silicon film at different hydrogen-dilution ratios was calculated according to Raman spectra. A 632.8 nm He–Ne laser was used in the Raman spectrometer, and the power of the incident beam was set below 50 mW to avoid thermally induced crystallization. The surface morphology of the silicon film, with different hydrogen-dilution ratios deposited on the COC substrate, was monitored using atomic force microscopy, and the scanning area was 1 × 1 μm in a tapping mode. The microstructure of the silicon film was observed using a scanning electron microscope (SEM) with cross-section and plane views.

### Fig. 1. Water vapor transmission rates of different polymer substrates.

<table>
<thead>
<tr>
<th>Type of polymer substrate</th>
<th>WVTR (g/m²-day)</th>
</tr>
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<tbody>
<tr>
<td>PC</td>
<td>7.741</td>
</tr>
<tr>
<td>PET</td>
<td>3.613</td>
</tr>
<tr>
<td>COC</td>
<td>1.141</td>
</tr>
<tr>
<td>Annealed COC</td>
<td>0.887</td>
</tr>
</tbody>
</table>

### Fig. 2. Raman spectra for silicon film deposited on COC substrates with (a) 0%, (b) 80%, (c) 90%, and (d) 95% hydrogen-dilution ratios.

### Fig. 3. SEM plan-view images of silicon film deposited on COC substrates with (a) 0%, (b) 60%, (c) 80%, and (d) 95% hydrogen-dilution ratios.

### Fig. 4. Roughness of coated silicon films on COC substrates with different hydrogen-dilution ratios.
3. Results and discussion

The Raman spectra of the silicon film deposited on a COC substrate with different hydrogen-dilution ratios are shown in Fig. 2. Silicon film with a 0% hydrogen-dilution ratio exhibited the broadest Raman peak at 480 cm\(^{-1}\), with a crystallinity of 0%; its amorphous features are shown in Fig. 2(a). The crystallinity of the silicon films could be changed from amorphous to microcrystalline as the hydrogen dilution changed. The Raman peak of silicon film with an 80% hydrogen-dilution ratio was located at 516 cm\(^{-1}\) and calculated to possess a crystallinity of 46.4%, as shown in Fig. 2(b). Silicon film with an 80% hydrogen-dilution ratio exhibited mixed microcrystalline and amorphous properties; this deposition produced a transition region of amorphous to microcrystalline features. However, the characteristics of silicon crystallinity at a particular hydrogen-dilution ratio can also be changed by applying high substrate [12] and filament temperatures [13]. In this study, incrementing the substrate and filament temperatures was not suitable for a polymer-flexible substrate because the radiation heat of the tungsten filament could curl the substrate. A high substrate temperature can cause the thermal accumulation of the polymer-flexible substrate to become deformed. The sharp peaks found near 520 cm\(^{-1}\), when the hydrogen-dilution values of the silicon films were higher than 90%, can be observed in Fig. 2(c) and (d). The crystallinity of the silicon films with hydrogen-dilution ratios of 90% and 95% were 53.7% and 77.6%, respectively.

The surface morphology of silicon films deposited on a COC substrate with different hydrogen-dilution ratios is shown in Fig. 3. Fig. 3(a) shows silicon film grown at a low substrate temperature by using pure silane gas; small grain particles were observed. Fig. 3(b)–(d) shows small grain particles clustering to form a larger grain particle as the hydrogen-dilution ratio increased. Fig. 3(d) shows the cluster grain particle clearly increasing when the hydrogen-dilution ratio reached 95%.

The surface roughness of silicon film deposited on a COC substrate with different hydrogen-dilution ratios is shown in Fig. 4. The roughness of silicon film with a 0% hydrogen-dilution ratio was 4.198 nm. The roughness of the silicon film with a 95% hydrogen dilution was 6.519 nm. The roughness of deposited silicon films increased as the hydrogen-dilution ratio increased; this result corresponded with the SEM image, as shown in Fig. 3.

The cross-section of the SEM image for silicon film with different dilution ratios is illustrated in Fig. 5. Amorphous tissue characteristics were observed in the silicon film with a 0% hydrogen-dilution ratio; no clear columnar crystalline characteristic was exhibited, as shown in Fig. 5(a). Silicon film with a 60% hydrogen-dilution ratio is depicted in Fig. 5(b). The columnar microstructure exhibited nanocrystallites embedded in an amorphous tissue. Fig. 5(c) shows the clear columnar crystallite characteristic of the silicon film with an 80% hydrogen-dilution ratio exhibited with an incremental width of elongated columnar crystallite. The elongated columnar crystallite changed to an inverted conic shape when the hydrogen-dilution ratio was increased to 95%, as shown in Fig. 5(d).

Fig. 6 shows the optical-absorption properties of silicon film with different hydrogen-dilution ratios: (a) photo conductivity, (b) dark conductivity, and (c) photosensitivity. The photo conductivity, as shown in Fig. 6(a), decreased from \(1.51 \times 10^{-2}\) to \(1.11 \times 10^{-9}\) \(\text{cm}^{-1}\) as the hydrogen-dilution ratio was increased. This phenomenon was also related to the crystallinity of the silicon films. Fig. 6(b) shows dark conductivity increased by one order of magnitude from \(6.51 \times 10^{-9}\) to \(3.89 \times 10^{-8}\) \(\text{cm}^{-1}\) when the hydrogen-dilution ratio increased from 0% to 95%. A low dark conductivity corresponded to preparing the amorphous silicon film using a 0% hydrogen-dilution ratio. Increasing dark conductivity corresponded clearly to the increasing crystallinity of the silicon films; its relationship with the Raman spectra is shown in Fig. 2. Fig. 6(c) shows the photosensitivity of the silicon films lowering as the hydrogen-dilution ratio increased. A maximal photosensitivity can be approached using a sample prepared at 0% hydrogen-dilution condition because an
amorphous silicon film has a higher absorption coefficient. Mahan et al. [14] considered a photosensitivity between $10^5$ and $10^6$ to be representative of an amorphous silicon film. In this study, a value of $2.3 \times 10^3$ meant an unoptimized amorphous silicon film prepared on a flexible substrate at a substrate temperature of 60 °C.

4. Conclusion

A lower WVTR in a flexible substrate could avoid the post-oxidization of silicon film when the silicon film is used to manufacture a flexible electronic device. When the hydrogen dilution is below 80%, a transition in the crystallinity of the silicon, from amorphous to microcrystalline, can be observed in a Raman spectrum. A conic-shaped crystal was formed when a sample was prepared at a 95% hydrogen dilution. The roughness of silicon was increased as the hydrogen-dilution ratio increased. The electrical properties of the silicon films were substantially affected by their crystallinity.

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References