CRYSTALLINE SILICON NITRIDE THIN FILMS GROWN BY PULSED YAG LASER DEPOSITION

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Abstract -- Silicon nitride (SiN) and silicon (Si) thin films have been prepared on Si (100) substrates using pulsed Nd:YAG laser (λ=532 nm) deposition. The laser beam is incident on the Si3N4 and Si targets. The films are grown using the energy density 3.8 J/cm² at a laser repetition rate of 10 Hz. The nitrogen gas pressure in the chamber is 10.0 Pa. The experiments have been done at different substrate temperatures. The films have been characterized by field-emission secondary electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR) and glancing angle X-ray diffraction (GXRD). FE-SEM shows that the SiN film consists of many particles whose sizes are about 200 - 600 nm. GXRD indicates that crystalline Si3N4 and Si thin films are obtained using Si3N4 and Si targets, respectively. ©1999 Acta Metallurgica Inc.

Introduction

Silicon nitride (Si3N4) is a compound that has applications in structural ceramics, high-temperature electronics, and tribology. Si3N4 can be used in extremely harsh environments because of its thermal, chemical, and mechanical stability. SiN films have been widely used in microelectronics for surface passivation and encapsulation in LSIs, as well as for gate insulator layers in thin-film transistors (TFTs) (1). Recently SiN films have been also used for membrane type bolometers (2,3). SiN films have been synthesized by a variety of techniques, including plasma-enhanced chemical vapor deposition (PE-CVD) (1), ion-beam assisted deposition (IBAD) (4) and pulsed laser deposition (PLD) (5). These films have been found to be mainly amorphous. In this paper, we describe a pulsed Nd:YAG laser deposition (PLD) process for the preparation of crystalline SiN and Si thin films and the characteristics of these films.
Experimental

A schematic illustration of the PLD apparatus used for this study is shown in Fig. 1 (6). As a light source we used a 532 nm pulsed YAG laser (Lumonics YM600) with a pulse width 6.5 ns. The laser beam was focused on the Si$_3$N$_4$ target (purity, 99.9%) and the Si target (purity, 99.999%), which were placed in the stainless deposition chamber at 45°. The laser energy density $E_{\text{L}}$ was fixed at 3.8 J/cm$^2$. The targets were rotated at about 20 rpm to avoid pitting of the target during the deposition. Single crystal Si (100) substrates of approx. 4 cm$^2$ area were ultrasonically cleaned in consecutive baths of ethanol and rinsing of high purity deionized water prior to loading in the deposition chamber. Prior to each deposition, the Si (100) substrates were sputter cleaned to remove any residual contamination. The Si (100) substrates were located at a distance of 60 mm from the facing target and were heated up to $T_s=700°C$ by an IR lamp. The gas pressure was varied from base pressure (below 4.0 x 10$^{-4}$ Pa) to 10.0 Pa (100% nitrogen). After 18000 to 36000 laser shots at a 10 Hz repetition rate, the deposition process was completed. The film thickness of 180 - 360 nm has been measured by an $\alpha$-step meter (KLA-tencor AS500). The deposition rate was about 6 nm/min. Table 1 shows the deposition conditions for the preparation of SiN thin films.

The surface morphology and structure of the SiN films were examined by field-emission secondary electron microscopy (FE-SEM; JEOL JSM-6300F) and Fourier transform infrared spectroscopy (FT-IR; JEOL JIR-5500), respectively. The crystalline structure and crystallographic orientation of the films were identified by glancing angle X-ray diffraction (GXRD; JEOL JDX3530) using CuK$\alpha$ radiation. The angle of incidence was kept at 1.0°.

Results and discussion

The surface morphology of SiN films on the Si (100) substrate was examined by FE-SEM seen in Fig. 2. The surface of this film, prepared at $P_{\text{gas}}=10.0$ Pa, $E_{\text{L}}=3.8$ J/cm$^2$, $d=6.0$ cm and $T_s=700°C$, consists of many rugged particles with sizes about 200 - 800 nm. Fig. 3 shows the FT-IR absorption spectrum of SiN thin film grown at $P_{\text{gas}}=10.0$ Pa and $T_s=700°C$. As can be seen in Fig. 3, absorption peaks appear at around 800 - 1200 cm$^{-1}$ and 450 - 600 cm$^{-1}$ due to the Si$_3$N$_4$ crystalline structure (7).
Table 1
Deposition Conditions for Si$_3$N$_4$ Thin Films

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser</td>
<td>Pulsed Nd:YAG laser</td>
</tr>
<tr>
<td></td>
<td>Wavelength $\lambda = 532$ nm</td>
</tr>
<tr>
<td></td>
<td>Pulsed width $\tau = 6.5$ ns</td>
</tr>
<tr>
<td></td>
<td>Energy density $E_p = 3.8$ J/cm$^2$</td>
</tr>
<tr>
<td></td>
<td>Repetition rate $f = 10$ Hz</td>
</tr>
<tr>
<td>Target</td>
<td>Si$_3$N$_4$ (purity 99.9%)</td>
</tr>
<tr>
<td></td>
<td>Si (purity 99.99%)</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>$d = 6.0$ cm</td>
</tr>
<tr>
<td>Rotating speed of the target</td>
<td>$\sim 20$ rpm</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si (100)</td>
</tr>
<tr>
<td>Ultimate pressure</td>
<td>$&lt; 4.0 \times 10^4$ Pa</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>$\sim 10.0$ Pa (100% Nitrogen)</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>$T_s = \text{room temp.} - 700^\circ C$</td>
</tr>
<tr>
<td>Deposition time</td>
<td>30 - 60 min</td>
</tr>
</tbody>
</table>

Detailed glancing angle X-ray diffraction measurements were carried out to study the crystalline properties of the laser deposited SiN films. Fig. 4 shows the XRD pattern of a reference target pellet of Si$_3$N$_4$. XRD patterns of as-deposited films grown at $P_{\text{N}_2}=10.0$ Pa and $T_s = 700^\circ C$ using Si$_3$N$_4$ and Si targets are shown in Fig. 5 and Fig. 6, respectively. When the Si$_3$N$_4$ target is used (Fig. 5), the X-ray reflections correspond to single phase polycrystalline Si$_3$N$_4$. For the sample deposited by the ablation of the Si target in a N$_2$ atmosphere (Fig. 6), there are only the distinct peaks of Si: (111), (220), (311), (400) and (331). The ratio of intensities of these peaks almost coincides with the diffraction pattern of an ideal Si powder, which indicates that this Si film has a nearly random polycrystalline structure. For samples deposited at room temperature using Si$_3$N$_4$ and Si targets, crystalline peaks of Si$_3$N$_4$ and Si also appear, respectively. Nevertheless, the crystalline quality of the Si film is better at a substrate temperature of $700^\circ C$.

Fig. 2 FE-SEM micrograph of the SiN film deposited at $P_{\text{N}_2}= 10.0$ Pa using a Si$_3$N$_4$ target ($E_p = 3.8$ J/cm$^2$, $d = 6.0$ cm, $T_s = 700^\circ C$).

Fig. 3 FT-IR absorption spectrum of the SiN film deposited at $T_s = 700^\circ C$ by using Si$_3$N$_4$ target ($P_{\text{N}_2}= 10.0$ Pa).

Fig. 4 $\theta - 2\theta$ X-ray diffraction pattern in CuK$\alpha$ radiation obtained from a Si$_3$N$_4$ target.
Conclusions

In this study, pulsed Nd:YAG laser deposition has been used to prepare appropriate crystalline SiN and Si thin films. The following results were obtained:

(1) Crystalline Si,N, thin films are obtained at substrate temperatures from room temp. - 700°C and a laser energy density of 3.8 J/cm² using a Si,N, target. The film surface morphology needs to be improved.

(2) High quality crystalline Si thin films are grown at substrate temperatures from room temp. - 700°C using a Si target.

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References