ON THE NANOCRYSTALLINE STRUCTURE OF TiC AND TiB₂ PRODUCED BY LASER ABLATION

I. Zergioti¹, G.N. Haidemenopoulos²

¹Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser, FORTH-IESL, P.O. Box 1527, 71110, Greece
²Department of Mechanical and Industrial Engineering, University of Thessaly, Volos 38334, Greece

(Accepted October 1996)

Abstract -- Thin films of TiC and TiB₂ have been deposited on silicon substrate by pulsed laser deposition technique, under substrate temperatures 25 - 600°C. Transmission electron microscopy revealed the nanocrystalline structure of the coatings. The grain size for the TiC film was between 10 and 70 nm and for the TiB₂ film was between 10 and 50 nm.

INTRODUCTION

The Pulsed Laser Deposition (PLD) process represents a method for growing high quality crystalline films (1). In this method, the laser beam is incident on a stoichiometric target and induces explosive evaporation of the material. The produced plasma acquires high kinetic energy and is deposited on the Si substrate which is placed parallel to the target. Among the advantages of the PLD technique over conventional film growth methods are the capability of obtaining stoichiometric films of multicomponent materials, the simplicity of the process, as well as the potential for refractory and ceramic film growth at low substrate temperatures.

Carbides and borides of transition metals exhibit unique physical and chemical properties and find a large number of applications in microelectronics and mechanical engineering. TiC and TiB₂ are refractory compounds (2) which combine ceramic properties, such as high melting point (3067°C, 3225°C), high hardness (2800HV, 3000HV), thermal and chemical stability, wear and corrosion resistance with metallic properties such as a low friction coefficient, and high electrical and thermal conductivity. Typical applications include high-performance cutting and forming tools, high corrosion resistance coatings for molten metal containers, thermal barriers in fusion and chemical reactors and diffusion barriers on Si in semiconductor technology.

Thin films of TiB₂ (3,4) and TiC (5,6) have been grown conventionally by chemical vapor deposition from the reactions of TiCl₄/C₂H₆, CCl₄, CH₄/H₂, and TiCl₄/BCl₃, B₂H₆/H₂, respectively under appropriate temperatures in the range of 800-1300°C. Molecular beam epitaxy and other sputtering techniques also require high growth temperatures (above 500°C). These temperatures can cause property changes and/or thermal damage in certain metallic substrates.
The need for a lower deposition temperature led to the development of other methods such as the laser-based deposition methods. Rist and Murray (7) reported the PLD of stoichiometric TiC on Si (100) substrates using a frequency doubled Nd:YAG laser at substrate temperatures between room temperature (RT) and 500°C. Donley et al. (8) investigated tribological properties of TiC films grown on 440°C stainless steel between RT and 300°C using excimer wavelengths.

In our previous work, TiC and TiB₂ have been deposited on steel and silicon (9). The aim of the present work was the investigation of the crystalline quality of these coatings. Emphasis was given to the transmission electron microscopy study of TiC and TiB₂ coatings on silicon substrates.

EXPERIMENTAL

Two types of TiB₂ raw materials were used in the experiments: commercially available pellets (d = 4.52 g/cm³) and hot-pressed pellets, sintered at 2500°C under controlled atmosphere (d = 3.5 g/cm³). TiC material was prepared by sintering at 2600°C (d = 4.58 g/cm³). The substrates used were silicon (100) wafers. Before deposition, the silicon substrates were cleaned to remove the surface oxide layer using 10% HF solution.

The experimental system consisted of a deposition chamber evacuated by means of a turbomolecular pumping system down to 10⁻⁶ mbar. The TiB₂ and TiC targets were irradiated at an incidence angle of 45° by the excimer laser (KrF at 248 nm, pulse duration 30 nsec). The beam was focused on the target using a plano convex lens of 300 mm focal length. The substrates were heated by an electric resistance and their temperature was measured by a thermocouple pressed directly onto the substrate surface.

The experimental parameters employed for the TiB₂ and TiC deposition are outlined in Table 1. The distance between the target and the substrate was 5 cm and the repetition rate of the laser was 20 Hz.

<table>
<thead>
<tr>
<th>Target</th>
<th>Substrate</th>
<th>Laser source</th>
<th>Energy density (J/cm²)</th>
<th>Irradiation time (min)</th>
<th>Substrate temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB₂</td>
<td>Silicon</td>
<td>KrF excimer</td>
<td>0.5</td>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>248 nm 30 nsec</td>
<td>1</td>
<td>12</td>
<td>300</td>
</tr>
<tr>
<td>TiC</td>
<td></td>
<td></td>
<td>1.5</td>
<td>15</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>20</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>20</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>20</td>
<td>600</td>
</tr>
</tbody>
</table>
Transmission electron microscopy was carried out using a JEOL JEM 120 CX. The TiC coatings on silicon were examined on the cross-section with the \{100\} Si plane parallel to the e-beam. The specimens were prepared by Ar ion beam thinning and were supported on 3 mm metallic rings.

**RESULTS AND DISCUSSION**

TEM analysis of the TiC coatings on Si revealed that fcc structure was grown with lattice constant \(a = 4.318\, \text{Å}\). Figure 1 depicts a bright field image and the associated diffraction pattern of the cross-section of the TiC coating on silicon deposited at 500°C substrate temperature. The zone axis \(<110>\) of the silicon and the diffraction rings of the polycrystalline TiC are depicted. It was observed that \(\{001\}\text{TiC}/\{001\}\text{Si}, \{110\}\text{TiC}/\{110\}\text{Si}, \{111\}\text{TiC}/\{111\}\text{Si} \) within approximately \(12°\).

Thus it can be concluded that the growth of the TiC film is epitaxial with the planes of the fcc structure of TiC almost parallel to the corresponding crystallographic planes of the Si substrate. The diffraction pattern of Figure 1 suggests the presence of texture in the coating. The TiC grains have grown parallel to the \([001]\) direction in a columnar growth manner. Observation of the bright-field image suggests that the interface between the coating and the substrate is cohesive without voids or linear defects.

Figures 2a and 2b depict a dark- and bright-field image respectively of the TiC coating. The dark-field image has been taken with the diffracted beam from the TiC diffraction rings. The grain size of TiC has been estimated in the range 10-70 nm.

TEM analysis of the TiB\(_2\) coatings of Si revealed that hexagonal TiB\(_2\) structure was grown with lattice constants \(a = b = 3.03\, \text{Å}, c = 3.23\, \text{Å}\) and \(\alpha = \beta = 90°, \gamma = 120°\). Figure 3 depicts the bright-field image and the associated diffraction pattern of the cross-section of the TiB\(_2\) on silicon, deposited at 600°C substrate temperature.

Figure 1. (a) Bright-field TEM micrograph of the cross-section of TiC coating on silicon and (b) the associated \(<110>\) Si electron diffraction pattern of the cross-section of the TiC coatings on Si substrate. FCC structure \((a = 4.318\, \text{Å})\).
Figure 2. (a) Dark-field and (b) bright-field TEM micrographs of granular TiC deposited at 500°C.

The zone axis $<110>$ and the diffraction rings of polycrystalline TiB$_2$ are revealed. It can be observed that $\{0001\}_{\text{TiB}_2}//\{001\}_\text{Si}$ and $\{1011\}_{\text{TiB}_2}//\{111\}_\text{Si}$ within 12°. This orientation relationship suggests that the growth of TiB$_2$ on Si is epitaxial, with the basal plane of the HCP structure grown parallel in the $\{001\}$ planes of the diamond type Si structure. The shape of the diffraction peaks of TiB$_2$ suggests the presence of texture with the TiB$_2$ grains grown parallel to the $<0001>$ direction in a columnar growth manner. The interface between the coating and substrate is cohesive and free of voids and linear defects. The grain size has been estimated between 10 nm and 50 nm.

Figure 3. (a) Bright-field of TEM micrographs of the cross-section of TiB$_2$ coatings on silicon deposited at 600°C and (b) the associated $<110>$ Si electron diffraction pattern of cross-section of the TiB$_2$ coatings. Hexagonal structure ($a = b = 3.03$ Å, $c = 3.23$ Å and $\alpha = \beta = 90°, \gamma = 120°$).
CONCLUSIONS

Nanocrystalline coatings of TiC and TiB$_2$ with grain size between 10 and 70 nm have been grown by pulsed laser deposition. In both cases the growth has been epitaxial on the (100) Si substrate while the films are textured due to columnar grain growth. The interface between coatings and substrate is cohesive and free of voids or linear defects.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance of CERECO for preparing TiC and TiB$_2$ targets, and the Large Installation Plan Ultraviolet Laser Facility at FORTH-IESL. This work was partially supported by the GSRT EPET II / 170 "Lasermat" project.

REFERENCES