DIAMOND-LIKE CARBON FILM PREPARATION AND SURFACE COATINGS OF OXIDE SUPERCONDUCTING AND FERROELECTRIC FILMS

SHIN-ICHI AQUKI,* KENJI EBIIHABA** and YUKIHIKO YAMAGATAb
aKumamoto Institute of Technology, Ikeda, Kumamoto, 860, Japan
bDepartment of Electrical and Computer Engineering, Kumamoto University, Kurokami, 2-39-1, Kumamoto, 860, Japan

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Abstract—Diamond-like carbon (DLC) films as well as amorphous carbon films are investigated as possible passivation and environment protection for YBaCuOx (YBCO) oxide superconducting and Pb(Zr,Ti,_,O3 (PZT) ferroelectric thin films. The pulsed laser deposition (PLD) technique was employed to prepare the perovskite oxide films of YBCO and PZT. These film surfaces were coated by the DLC films prepared using the excimer laser ablation method. Optimun deposition condition of the PLD process for the YBCO, PZT and DLC was investigated. In the case of DLC coatings, a graphite target was ablated using a KrF excimer laser of 2-9 J cm⁻² in 200-800 mTorr hydrogen ambient gas. An optical band gap of 2.0 eV was attained on room temperature substrate and high quality superconductivity of the DLC coated YBCO films was kept over 1 month. The PZT film encapsulated by the DLC layer showed no degradation due to aging over 30 days. © 1998 Elsevier Science Ltd. All rights reserved.

Key Words—A. Diamond-like carbon, B. coating, C. optical properties.

1. INTRODUCTION

Carbon based thin films have attracted much attention due to their promising electronic devices, optical passivation coating and heterostructure for advanced versatile devices. The diamond-like carbon (DLC) films have excellent combinations of physical hardness, optical transparency, high thermal conductivity and electrical insulation. High-quality oxide films such as high-Tc superconductors and ferroelectrics degrade by exposure to atmosphere. The DLC films as well as amorphous carbon films have been investigated as possible protective layers for YBaCuOx (YBCO) [1]. Ferroelectric thin films have a broad range of applications owing to their multiple electrical, electro-optic and piezoelectric properties and also due to the possibility of heterostructure with high-Tc superconductor devices. Lead zirconia–titanate [Pb(Zr,Ti,_,)O3; PZT] is a perovskite-type ferroelectric material which is one of the most promising materials for a radiation-hardened nonvolatile memory and storage capacitor in high-density dynamic random access memory. The PZT has a high dielectric constant and a good lattice matching to YBCO. The high-Tc superconducting field effect devices based on the metal-insulator–YBCO films where PZT is used as a gate insulator have been investigated [2].

Many processes including plasma chemical vapor deposition (CVD), plasma sputtering, electron beam process, thermal plasma process have been attempted for preparing the high-quality carbon based thin films. Pulsed laser deposition (PLD) has been used to prepare a variety of thin films, from high-Tc oxide superconducting films to many versatile films such as oxide, nitride and heterostructures composed of multilayers.

This paper studies the preparation of the high quality DLC thin films using the excimer laser ablation technique. The film properties of the deposited DLC films were investigated by means of infrared (IR) absorption and visible light spectrometer. The DLC thin films were also used to coat the surface of the oxide thin films (YBCO,PZT). The electrical characteristics before and after encapsulation by a DLC layer was investigated regarding the quality degradation due to aging.

2. EXPERIMENTAL

The DLC films were deposited by KrF excimer laser (λ = 248 nm, pulse width 25 ns) ablation of a rotating graphite target (φ 30 mm × 5 mm, 99.999% purity) [3]. The pure hydrogen gas was fed into the chamber (φ 500 mm × 40 mm, stainless) after evacuating to a base pressure of 5 × 10⁻⁷ Torr. A KrF laser beam (Lambda Physik Model LPX305ic, maximum energy 1200 mJ) was introduced into the chamber through lenses and fused quartz window. The laser energy density from 2 to 9 J cm⁻² was made incident on the small area (2 × 5 mm²) of the pellet at an angle of 45°.

Initial experiments were carried out to estimate the process parameters for DLC film preparation. The
DLC single layer was deposited on substrates such as quartz, Si(100) and MgO(100). In order to estimate optimum deposition conditions, DLC films were prepared under various parameters of laser energy density, repetition frequency, ambient hydrogen pressure and the distance between the target and the substrate. Table 1 shows the experimental conditions for DLC film preparation. Optical transparency and the optical band gap of the DLC films were measured by using a visible light spectrometer. The bonding structure was also investigated with a Fourier transform infrared (FTIR) spectrometer.

The protective DLC coatings for the superconducting YBCO films and the ferroelectric PZT films were followed. YBCO films were deposited on the MgO(100) substrate heated to 710°C. Typical laser energy density of 3 J cm⁻² was irradiated on the sintered bulk YBCO target. PZT thin films were prepared on the YBCO films deposited on the MgO substrate. The conducting YBCO layer is selected as the bottom electrode for the capacitive structure. The heterostructure PZT/YBCO/MgO was used to measure the electrical properties of the ferroelectric PZT. The deposition conditions for YBCO and PZT films were shown in Table 2. The oxide films were characterized using X-ray diffraction, scanning electron microscopy and electron probe microanalysis. Four-terminal resistance measurements were made to study the superconducting transition. The ferroelectric properties like the polarization-electric field strength hysteresis loop were obtained using the Sawyer–Tower measurement.

### Table 1. Experimental condition for DLC film preparation

<table>
<thead>
<tr>
<th>Laser energy density (J cm⁻²)</th>
<th>9</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetition rate (Hz)</td>
<td>10</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Target</td>
<td>Graphite</td>
<td>PZT</td>
<td>YBCO</td>
</tr>
<tr>
<td>Substrate</td>
<td>Quartz, Si(100), MgO(100) at room temperature</td>
<td>Si(100)</td>
<td>MgO</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>25°C</td>
<td>750°C</td>
<td>710°C</td>
</tr>
<tr>
<td>Ambient gas</td>
<td>Hydrogen</td>
<td>Oxygen</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>200</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>200</td>
<td>400</td>
<td>200</td>
</tr>
</tbody>
</table>

### Table 2. Deposition conditions for DLC, PZT and YBCO layers of the Au/DLC/PZT/YBCO/MgO structure

3. RESULTS AND DISCUSSION

#### 3.1 Diamond-like carbon film preparation

The deposited films have been formed from opaque to transparent depending on the process conditions. Typical optical transparency and the Tauc plot are shown in Fig. 1(a and b), respectively. This sample was deposited on the quartz substrate at room temperature (25°C). The laser energy density of 8 J cm⁻² with a repetition rate of 10 Hz at 800 mTorr H₂ was used. The film thickness of 300 nm was obtained by the 12 000 laser shots. The Tauc plot indicates that the DLC film has an optical band gap $E_{opt}$ of 2.0 eV. This result shows that the excimer laser ablation process can provide high optical band gap at low process temperature. Figure 2 shows the optical band gap as a function of laser energy density for the DLC films deposited at a hydrogen pressure of 200 mTorr. The $E_{opt}$ increases with increasing the laser energy and attains a maximum value of 2 eV. The ambient pressure of hydrogen gas did not give remarkable effect on the $E_{opt}$ when the pressure in the range of 200–800 mTorr was chosen.

Figure 3 shows the IR absorption spectrum of the film deposited at the same condition as in Fig. 1. A strong peak was observed for $sp^3$ CH₂ mode at 2925 cm⁻¹ which is attributed to diamond-like char-
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Fig. 2. The optical band gap $E_{opt}$ as a function of laser energy density at a hydrogen pressure of 200 mTorr.

Fig. 3. The IR absorption spectrum of film deposited at 8 J cm$^{-2}$ and 800 mTorr.

3.2 DLC protecting coating for superconducting YBCO films

Environmental degradation of the oxide superconductor will reduce the critical zero resistivity temperature $T_{cero}$ as well as the critical electric current density $J_c$. The use of DLC films has been investigated for protecting YBCO films against degradation from exposure to moisture and acid [1,4]. The encapsulated film showed no degradation due to acid treatment or aging over a period of 45 days [1].

The protective effect of the DLC coating layer on the superconducting properties for YBCO thin films has been studied [5]. Figure 4 shows the resistance versus temperature curve of the YBCO film coated by the DLC thin film. The DLC film was deposited on the YBCO/MgO(100) substrate with a laser energy density of 4 J cm$^{-2}$ at a repetition frequency of 5 Hz. It is found that the small degradation appears after 20 days aging while there is no remarkable reduction of superconducting properties in first 4 days. It is shown that the aging degradation reduces the electric conductivity and $J_c$, but that it does not change the value of $T_{cero}$.

3.3 DLC encapsulation of heterostructure PZT–YBCO

Ferroelectric thin films offer new promising applications including non volatile memories, dynamic random access memories and electro-optic devices. It has been suggested that the superconductive cuprate may be a better oxide electrode candidate for ferroelectric memory devices than the traditional Pt metal electrode [6]. However, the ferroelectric properties of the PZT–YBCO structure show degradation due to removal of oxygen atoms in the film and interface interdiffusion. The heterostructure was coated by the DLC thin film in order to prevent from degrading the physical properties in the atmospheric ambient. A heterostructure Au/DLC/PZT/YBCO/MgO was fabricated. The X-ray diffraction patterns showed that the PZT films prepared on YBCO/MgO(100) substrate at 550–680°C have a perovskite (001) structure. Figure 5 shows the polarization-electric field hysteresis loops of DLC protected and uncoated PZT–YBCO/MgO structures measured by a Sawyer–Tower circuit at 1 kHz. The protected PZT film in this heterostructure exhibits dielectric hysteresis with remnant polarization of 6 C cm$^{-2}$ which is ca 40% smaller than the remnant polarization of uncoated film. But, the coercive field strength (width: 100 kV cm$^{-1}$) does not show remarkable reduction due to DLC protection coating. The specific dielectric constant was in the range of
700–800°C. This encapsulated PZT film showed no degradation due to aging over a period of 30 days.

4. CONCLUSION

The excimer laser ablation process provides high quality DLC films at room temperature. The deposited films show the wide optical band gap of ca. 2 eV and good adhesion to the quartz substrate. The DLC encapsulation for the YBCO superconducting thin films and the ferroelectric heterostructure PZT–YBCO showed no degradation due to aging over a period of 1 month.

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