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Diamond-like carbon film deposition on PZT ferroelectrics and YBCO superconducting films using KrF excimer laser deposition

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Abstract

Ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) and superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) thin films were coated by unhydrogenated diamond-like carbon (DLC) films in order to reduce the aging degradation. Excimer laser ablation technique is applied to prepare PZT, YBCO and DLC films. The 60 days aging degradation of the DLC coated YBCO structure is limited within only 10% decay of normal resistivity. The polarization-electric field characteristics of the ferroelectric capacitor Au/PZT/YBCO/MgO shows a remanent polarization of 23.2 μC/cm^2 and a coercive field of 54.0 kV/cm. At least 10% decay of these ferroelectric values was observed after 60 days exposure to atmosphere.

Keywords: Diamond-like carbon

1. Introduction

Carbon films consisting of sp^2 graphitic carbon and sp^3 hybridized carbon bonding have the unique properties depending on the deposition parameters of various processing techniques. The amorphous graphitic carbon (a-C) films are electrical conductors containing high fraction of sp^2-bond phases. On the other hand, diamond-like carbon (DLC) films have high electrical resistivity and breakdown field and optical transparency over a wide optical spectral range. a-C and DLC films also show large thermal conductivity, chemical inertness and high hardness. The deposited films can exist in a continuum of states between above two extreme states. All of above properties are suitable for coating materials in microelectronics as well as in mechanical applications. Recent research of field electron emission devices opens new attractive applications using a-C and DLC films [1]. Among the various methods for depositing carbon films, pulsed laser deposition has been shown to be one of the most attractive techniques.

We have deposited carbon films by means of KrF excimer laser ablation method. The pervious report shows that the deposited DLC films have wide optical band gap of about 2 eV and good adhesion to the quartz substrate [2]. The spectroscopic measurements of the KrF excimer laser ablated plasma plume indicate that at the H_2 atmosphere, there are neutral and ionic species such as H, C, C^+, CH, CH^+, C_2H and C_2H^+. The properties of the deposited films are strongly affected by laser plasma plume dynamics.

We study here the DLC film deposition on the PZT ferroelectrics films as well as YBCO superconducting films. PZT films have excellent ferroelectric, optical and piezoelectric properties. Recently, PZT thin films have been studied extensively for nonvolatile memory devices. These devices undergo a large amount of read/write cycles in order to retrieve/store information and thus the integrated ferroelectric/semiconductor devices require long-term reliability including fatigue, retention, and imprint. YBCO films have been widely used to investigate various aspects of the oxide superconductor systems. This form of the high T_c superconductor is applicable for microelectronic devices including superconducting quantum interference devices (SQUID), microwave filters and interconnects. In oxide perovskite materials such as PZT and YBCO, oxygen and related defects are believed to play an important role on electrical/crystallographic properties and the reliability. Degradation of the oxide materials by exposure to atmospheric environment has been one of the continuing concerns limiting the effective use of these attractive materials. In this paper, the DLC, PZT and YBCO films are deposited using KrF excimer laser process. Environmental degradation for the PZT/YBCO and DLC/YBCO structures has been studied using the Sawyer–Tower measurements, X-ray diffraction, scanning electron microscopy, electron probe microanalysis and four-terminal resistance measurement.

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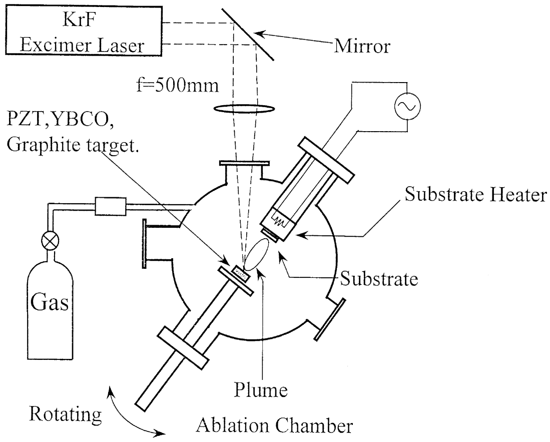

Fig. 1. Schematic of the KrF excimer laser ablation system.

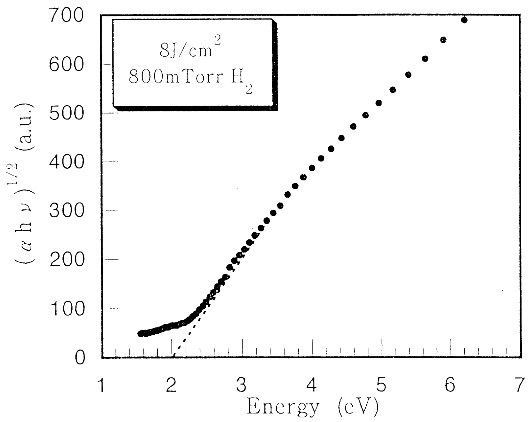

Fig. 2. Tauc plot for hydrogenated DLC film prepared on the quartz substrate.

2. Experimental study

Fig. 1 shows a schematic diagram of the KrF excimer laser ablation system used in the present study.

The DLC films were deposited by KrF excimer laser ($\lambda = 248$ nm, pulse width 20 ns) ablation of a rotating graphite target (ϕ30 mm $\times$ 5 mm, 99.999% purity) [3]. Pure hydrogen or helium gas was fed into the chamber (ϕ500 mm $\times$ 400 mm, stainless) after evacuating to a base pressure of 5×10^{-7} Torr. A KrF laser beam (Lambda Physik Model LPX305icc, maximum energy 1200 mJ) was introduced into the chamber through lenses and fused quartz window. The laser beam was focused onto the small area (2×5 mm^2) of the pellet at an incident angle of 45°. The laser fluence on the target was in the range of 2–9 J/cm^2 and was obtained by varying the operating parameters of the laser system. The DLC single layer was deposited on substrates such as quartz, Si(100) and MgO(100). Optimum deposition conditions for the DLC films were studied under various parameters of laser energy density, repetition frequency, ambient gas pressure and the distance between the target and the substrate. Optical transparency and the optical band gap of the DLC films were measured by using a visible light spectrometer (SHIMADZU UV-160). The bonding structure was also investigated with a FTIR spectrometer (SHIMADZU 8200A).

The DLC surface coatings for the ferroelectric PZT films and the superconducting YBCO films were performed. Details of the deposition conditions for PZT and YBCO are described elsewhere [4,5]. Table 1 gives the deposition conditions for YBCO and PZT films. YBCO films were deposited on the MgO(100) substrate heated to 710°C with a typical laser energy density of 2 J/cm^2. The resistivity versus temperature measurements were used to estimate superconducting properties of the YBCO films.

PZT thin films were deposited on the YBCO film prepared on MgO or YAlO substrates. The conducting YBCO layer is selected as the bottom electrode for the ferroelectric capacitive structure. The heterostructure PZT/YBCO/MgO or YAlO was used to measure the electrical properties of the ferroelectric PZT. The ferroelectric properties like the polarization-electric field strength hysteresis loop were obtained using the Sawyer–Tower measurement. The fatigue behavior for 10^{10} cycles of 20 V_{p-p} at 1 kHz was studied.

3. Results and discussion

The deposited carbon films varied from opaque to transparent depending on the process conditions. The Tauc plot for the sample prepared at optimum conditions shows an

Table 1
Deposition conditions for YBCO and PZT films

Film	YBCO	PZT
Laser	KrF excimer laser	KrF excimer laser
Energy density (J/cm^2)	2	2
Repetition rate (Hz)	5	5
Laser shot	3700	3600
Target	$YBa_2Cu_3O_{7-x}$	$PbZr_{0.52}Ti_{0.48}O_3$
Substrate	MgO, YAlO	YBCO/MgO, YBCO/YAlO
Substrate temperature (°C)	710	550
Ambient gas pressure (mTorr)	O_2:200	O_2:100
Annealing	–	O_2:600 Torr, 400°C, 60 min

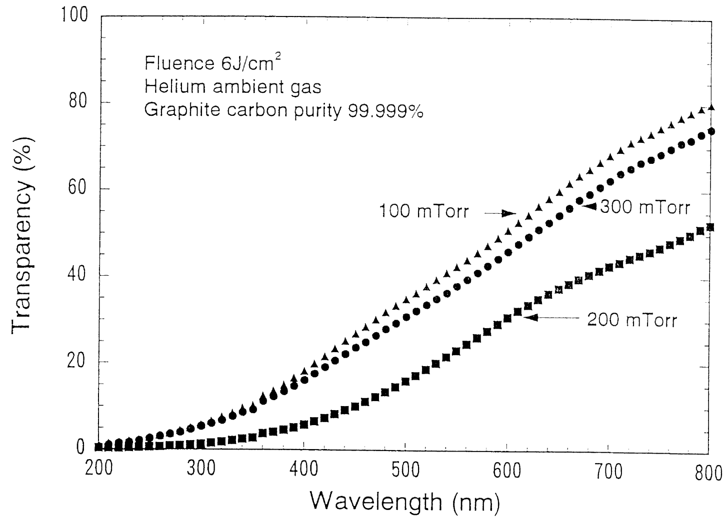

Fig. 3. Optical transparency of tetrahedral amorphous carbon (ta-C) films deposited at various helium pressures.

optical band gap E_{opt} of 2.0 eV as shown in Fig. 2. This sample was deposited on the quartz substrate at room temperature (25°C). A laser energy density of 8 J/cm^2 with a repetition rate of 10 Hz at 800 mTorr H_2 was used. A film thickness of 300 nm was obtained by the 12 000 laser shots. This result shows that the excimer laser ablation process can provide high optical band gap at low process temperature. The FTIR absorption measurements show a strong peak for sp^3 CH_2 mode at 2925 cm^{-1} which is attributed to diamond-like character. The deposited films under the condition (8 J/cm^2, 10 Hz, 800 mTorr) predominantly consisted of sp^3-bonded C.

Tetrahedral amorphous carbon (ta-C) films with no incorporated hydrogen are of considerable interest, because of their high hardness and substitutional doping capability compared with hydrogenated DLC film [6]. The ta-C film having a high sp^3 content shows more diamond-like character. Cuomo et al. showed that the pulsed laser ablation method provides improved diamond-like carbon films [7]. Surface coating by the DLC (ta-C) films can reduce the interface reaction between activated species contained in the coating layer and the incorporated oxygen in the oxide films. We prepared the DLC(ta-C) films for surface coating of the YBCO and PZT films. The DLC(ta-C) films deposited under helium gas have higher hardness than the DLC films prepared under hydrogen ambient gas while the optical energy band gap of the ta-C is lower than that of hydrogenated DLC film. Typical optical property for DLC(ta-C) films is shown in Fig. 3. These films were prepared on quartz substrates at various pressures of helium under the deposition conditions indicated in Table 2. The Tauc plot for the 200 mTorr film provides an optical band gap energy of 1.0 eV.

Table 2
Deposition conditions for YBCO and DLC(ta-C) films

	YBCO	DLC(ta-C)
Laser	2 J/cm^2, 5 Hz	8 J/cm^2, 10 Hz
Target	$YBa_2Cu_3O_{7-x}$	Graphite carbon (99.999%)
Gas	O_2 200 mTorr	He 300 mTorr
Substrate	MgO	YBCO/MgO
Temperature	710°C	Room temperature
Shots	3000 shots (300 nm)	9000 shots (300 nm)

The DLC surface coating has a strong influence on the ferroelectric and superconducting properties of the samples. The DLC(ta-C) films are used as the surface coating material. Fig. 4 presents the resistivity versus temperature curves for the YBCO/MgO film. The sample shows initial superconducting transition at T_c(zero) = 83.0 K and T_c(onset) = 85.0 K immediately after the film preparation. The superconducting properties gradually change with time. Although T_c(zero) shows small rise of about 3 K during 30 days, normal resistivity at 300 K indicates 110% increase after 30 days. The normal resistivity (ρ_n) of the YBCO superconductor at room temperature reflects electronic properties due to the aging degradation because ρ_n is expressed by $m/(n_n e^2 \tau)$ where n_n is the normal electron density, m is the effective mass and τ the relaxation time. The initial degradation of these oxide films is considered to be mainly caused by removal of oxygen atoms in the films and interface diffusion.

Fig. 5 indicates that the DLC coated YBCO film shows slight change in the normal resistivity. However, the remarkable degradation accompanied by the DLC surface coating does not appear on the superconducting transition such as T_c(zero) and T_c(onset). The long-term degradation (60 days) of the DLC/YBCO/MgO sample is limited within only 10% increase of normal resistivity.

It has been reported that the PZT ferroelectric thin films with conducting YBCO oxide electrode yield better fatigue characteristics than those with Pt electrodes [8]. In this paper, the ferroelectric properties as well as the superconducting properties for the PZT/YBCO/MgO film are

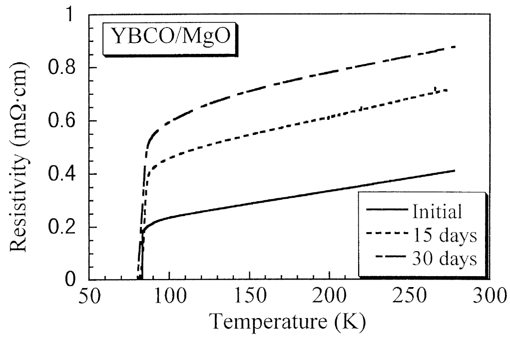

Fig. 4. Aging degradation of resistivity versus temperature characteristics for the YBCO/MgO film.

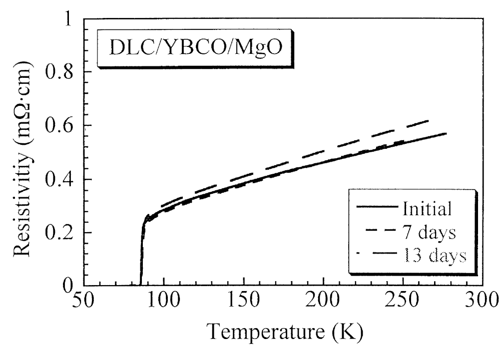

Fig. 5. Resistivity versus temperature characteristics of the unhydrogenated DLC film exposed to atmospheric environment.

studied. Fig. 6 is a heterostructure for measuring the polarization (P) versus electric field (E) characteristics. Au dots of diameter 200 μm were used as the top electrode. The triangular voltage wave (20 V_{p-p}) operated at 1 kHz was applied between YBCO and Au electrodes. Fig. 7 is the P–E hysteresis curves when the sample was exposed to atmospheric environment over 20 days. It is found that the sample initially shows a remanent polarization (P_r) of 23.2 μC/cm^2 and a coercive field (E_c) of 54.0 kV/cm. After 20 days exposure to atmosphere, the remanent polarization and the coercive field of the PZT sample decayed to 95% at the initial ferroelectric parameters. Fig. 8 shows the aging degradation of spontaneous polarization (P_s), remanent polarization and coercive field. P_r dropped about 10%

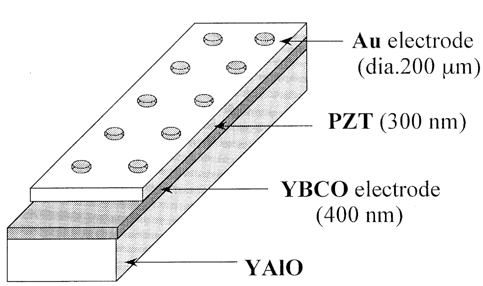

Fig. 6. The Au/PZT/YBCO/YAlO capacitive structure.

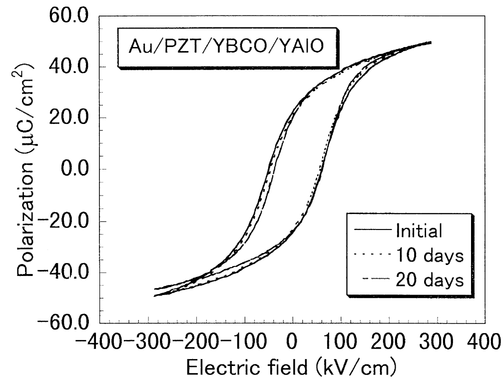

Fig. 7. Degradation of the ferroelectric hysteresis loops of Au/PZT/YBCO/YAlO structure.

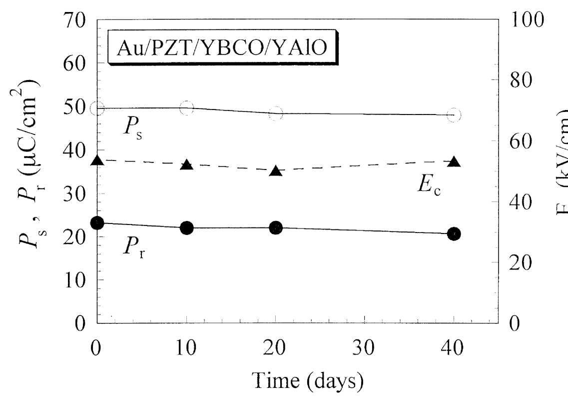

Fig. 8. Spontaneous polarization (P_s), remanent polarization (P_r) and coercive field (E_c) of the Au/PZT/YBCO/YAlO structure as a function of time (days).

after 40 days but we observed only a few % decrease for P_s and E_c.

Fig. 9 shows the remanent polarization as a function of fatigue cycles at room temperature. These fatigue measurements were carried out at a cycle frequency of 50 kHz. The

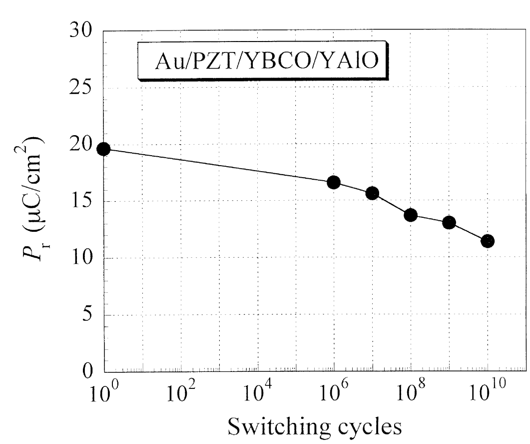

Fig. 9. Remanent polarization versus fatigue cycles for Au/PZT/YBCO/YAlO capacitive structure.

polarization shows about 15% decay after 10^6 cycles and then drops to 60% at 10^{10} cycles.

4. Conclusions

We have studied the aging and fatigue degradation of superconducting YBCO and ferroelectric PZT films for superconducting field effect devices and nonvolatile memory devices. In order to maintain superconducting and ferroelectric properties of the oxide films prepared by the excimer laser ablation method, unhydrogenated tetrahedral amorphous carbon DLC (ta-C) film is shown to be promising surface coating candidate. The ta-C coated YBCO films do not show remarkable degradation of superconducting transition after 13 days while degradation of its normal resistivity is limited to within 10% increase after 60 days exposure to atmospheric environment. The PZT/YBCO heterostructure shows high quality ferroelectric properties with a remanent polarization of 23.2 $\mu C/cm^2$ and a coercive field of 54.0 kV/cm. The DLC coating on this structure degrades the ferroelectric properties and low permittivity of the DLC film affects the characteristics of the ferroelectric devices.

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