Vol 18 No 4, April 2009
1674-1056/2009/18(04)/1679-05

Chinese Physics B

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A comparative study of $YBa_2Cu_3O_{7-\delta}$/YSZ bilayer films deposited on silicon-on-insulator substrates with and without HF pretreatment*

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(Received 24 November 2008; revised manuscript received 18 December 2008)

Highly epitaxial $YBa_2Cu_3O_{7-\delta}$ (YBCO) and yttria-stabilized zirconia (YSZ) bilayer thin films have been deposited on silicon-on-insulator (SOI) substrates by using *in situ* pulsed laser deposition (PLD) technique. In the experiment, the native amorphous SiO_2 layers on some of the SOI substrates are removed by dipping them in a 10% HF solution for 15 s. Comparing several qualities of films grown on substrates with or without HF pretreatment, such as thin film crystallinity, general surface roughness, temperature dependence of resistance, surface morphology, as well as average crack spacing and crack width, naturally leads to the conclusion that preserving the native SiO_2 layer on the surface of the SOI substrate can not only simplify the experimental process but can also achieve fairly high quality YSZ and YBCO thin films.

Keywords: pulsed laser deposition, thin film, pretreatment, SOI substrate
PACC: 8115I, 6855

1. Introduction

Silicon wafers are the cornerstone of the semiconductor industry because of their perfect crystallinity, smooth surface, large area, low price, and appropriate dielectric properties. Great efforts have been made to deposit various kinds of novel functional thin films, especially high temperature superconductors (HTSC), on Si wafers in order to reach a thorough integration of the oxide devices for practical applications in semiconductor industry.[1−8] Recently, silicon-on-insulator (SOI) substrates have become a new highlight in the semiconductor field, which reduce parasitic device capacitance, and thereby improving performance.[9] This SOI substrate differs from conventional Si wafers with a buried oxide layer, but it still has about 2-nm-thick native amorphous silicon oxides (mainly SiO_2) on the surface, as conventional Si wafers have, which makes the nucleation of epitaxial oxide thin films difficult. Up to now, three techniques have been developed to remove the surface SiO_2 layer. The first one is annealing in ultra high vacuum (better than 2×10^{-10} Torr) (1 Torr = 133 Pa) at 870 °C for 15 min,[10] the second one is sputtering by Ar^+-ion at a low energy of 1 keV and a low temperature for a few minutes,[11] and the last one is chemical treating. From among them the well accepted and most effective method is the chemical treating called "spin-etching". A few drops of etchant ($HF:H_2O:CH_3CH_2OH = 1:1:10$) are dripped onto the surface of a wafer rotating at a high speed. The resulting hydrogen-terminating surface prevents Si from being reoxidized in air and is maintained until the substrate is heated to above 400 °C.[12] However, lately Pechen *et al*[13] and Wang *et al*[14] have successfully prepared high quality epitaxial $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films with different buffer layers directly on pristine Si wafers, which greatly simplifies the film growth process. Moreover, the results obtained from x-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM) show that the native amorphous SiO_2 layer is removed completely along with the

*Project supported by the National Natural Science Foundation of China (Grant Nos 50672125 and 10574154), the Natural Science Foundation of Shanxi Province, China (Grant No 2009011003-1), and the Youth Foundation of Shanxi Datong University, China (Grant No 2007Q10).
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continuous deposition of YSZ at a low ambient oxygen pressure and high temperature.[14] In the present paper, we report on the growth of epitaxial YSZ and YBCO bilayers on SOI substrates with and without the amorphous SiO_2 layer and mainly focus on a detailed comparison between the film qualities. For convenience we simply dipped the SOI substrate in the etchant for several seconds and then rinsed in de-ionized water, instead of using spin-etching. We found that YSZ and YBCO thin films grown on pristine SOI substrates were as good as, if not better than, that grown on HF pretreated SOI substrates.

2. Experimental details

The structural parameters of the SOI wafer we adopted have been described in the previous paper.[15] In this work, we used two different methods to pretreat the SOI substrates. Some of the substrates were ultrasonically cleaned in diluted phosphoric acid (4%), de-ionized water, alcohol and acetone sequentially. In this way organic contaminations could be removed from the substrate surface while the native amorphous SiO_2 layer remained there. The rest were dipped in diluted HF (10%) solution for 15 s to remove the amorphous SiO_2 layer followed by the above-mentioned conventional cleaning process. Subsequently, we rapidly sent the heater loaded with SOI substrates into a vacuum chamber and kept the background pressure below 10^{-3} Pa during the heating process to avoid further oxidization. We deposited *in situ* YBCO/YSZ bilayer films on the two kinds of SOI substrates under the same deposition conditions by using the pulsed laser deposition (PLD) method. The details of the growth conditions and characterizations of the bilayer thin films have been described elsewhere.[15] The film growth rate was about 5 nm per minute for YSZ and 13 nm per minute for YBCO.

The film crystallinity and orientation were monitored *in situ* by using a home-made reflection high energy electron diffraction (RHEED) system with an acceleration voltage of 25 kV ($\lambda_{el} \approx 0.0076$ nm). The ω-scan (rocking curve) using a four-circle diffractometer with a Cu K_α source was performed to quantitatively characterize the crystallinity of the films. Atomic force microscopy (AFM, Autoprobe CP) was used to obtain the information about the film surface roughness. The resistance-temperature curves of YBCO thin films were measured by using a standard four-probe method. The surface morphologies, crack widths and average crack spacings of YBCO thin films were investigated by scanning electron microscopy (SEM, XL30S-FEG).

3. Results and discussion

For convenience, in the following discussion the YBCO/YSZ bilayers grown on SOI substrates reserving the native SiO_2 layer were assigned as sample 1, and those on HF pretreated SOI substrates as sample 2.

Figure 1 shows the *in situ* RHEED patterns of the two samples. The images a, b and c are for the SOI substrates, YSZ and YBCO thin films, respectively. The electron beam was along the SOI [100] direction. The subscripts 1 and 2 denote samples 1 and 2 respectively. Figures 1(a_1) and 1(a_2) were taken at room temperature in high vacuum. The diffraction spots are located on the Laue circle and clear Kikuchi lines are also observed, suggesting that the substrates are rather perfect with high crystallinity and good smoothness. Nevertheless, we notice that the pattern in Fig.1(a_2) is clearer, sharper and more vivid than that in Fig.1(a_1). It is well known that RHEED is very sensitive to the sample surface, especially the top few atomic layers. Therefore, the better pattern in Fig.1(a_2) can be ascribed to the removal of the native amorphous SiO_2 layer, which increases the "visibility" of the top Si layer on the SOI substrate. However, weak short rods as a signature of a three-dimensional (3D) diffraction also appear in Fig.1(a_2) other than the bright spots on Laue circle, revealing a rougher substrate surface. The RHEED pattern of an SOI substrate dipped in HF solution for 60 minutes has an obvious 3D feature (not shown here). Similar phenomenon was reported by Kawasaki *et al.*[16] Therefore by dipping in the diluted HF solution many tiny corrosion steps occur on the SOI substrate surface, which increase the surface roughness. The more the dipping time is, the rougher the substrate surface will be. Figures 1(b_1) and 1(b_2) are taken after 10 min deposition at the growth temperature in high vacuum (5×10^{-4} Pa). Because an RHEED diffraction pattern is the intersection of 2D reciprocal rods with the Ewald sphere, the bright and clear diffraction streaks instead of round spots shown here are due to the finite size of the rods, therefore implying that the surfaces of the YSZ films are 2D-like smooth

and the quality of in-plane epitaxy is good. These are advantageous to the following growth of YBCO thin films. Patterns of YBCO thin films taken after 15 min deposition at room temperature in high vacuum are shown in Figs.1(c_1) and 1(c_2). Similarly, sharp and bright streak-like patterns reveal a smooth surface and a good crystallinity of the YBCO thin films deposited on YSZ buffer layers.

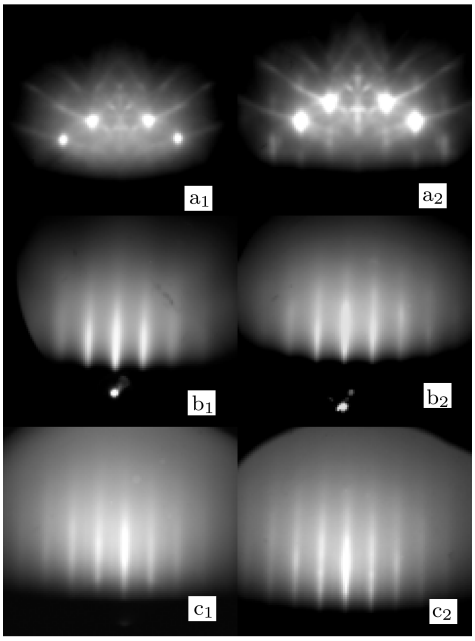


Fig.1. RHEED patterns of (a) SOI substrates, (b) YSZ thin films after 10-minute deposition and (c) YBCO thin films after 15-minute deposition, where subscripts 1 and 2 denote samples 1 and 2 respectively and the electron beam is along the SOI [100] direction.

Because RHEED observations can reveal only the crystallinity and the surface morphology of the films qualitatively, we also do rocking curve and AFM measurements in order to compare the qualities of the two samples quantitatively. Figure 2(a) is the rocking curves of YSZ (002) peaks appearing at 34.78°. The full widths at half maximum (FWHMs) are 0.67° for sample 1 and 0.91° for sample 2. It is evident that the crystallinity of YSZ film in sample 1 is better than that in sample 2. Moreover, we grew another YSZ thin film on an SOI substrate that had dipped in HF solution for 60 minutes, whose FWHM is up to 1.17°. Therefore, the obvious difference in FWHM of rocking curve between the two samples can be attributed to the appearance of tiny corrosion steps on the surface of the later. In view of the theory, anti-phase grain boundaries or misoriented grains are more easily formed on the step edges than in smooth surfaces, which well explains the worse crystallinity of YSZ thin film in sample 2. Meanwhile, the rocking curves of YBCO (005) peaks appearing at 38.53° are shown in Fig.2(b). The values of FWHM are 1.34° and 1.28° for samples 1 and 2, respectively. That is to say, the crystallinity of YBCO films is equivalent for the two samples. This might suggest that the crystallinity of YBCO films is little affected by the substrate pretreating method because of the existence of the YSZ buffer layer.

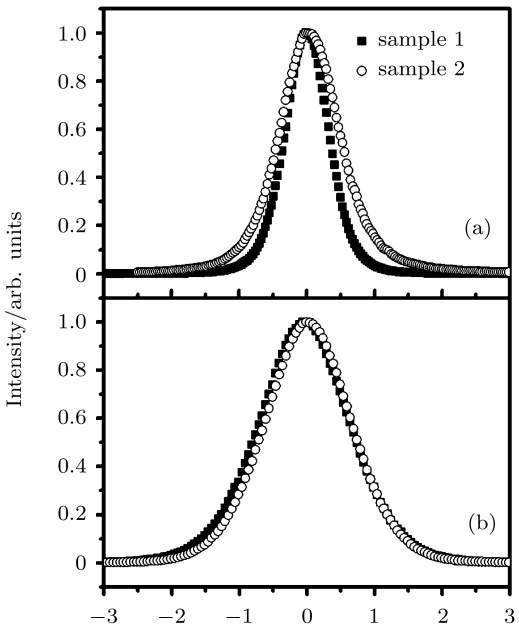


Fig.2. Rocking curves of YSZ (002) peaks (a) and YBCO (005) peaks (b) of the two samples.

The root-mean-square roughness (R_q) and the average roughness (A_v) in an area $5\times5\,\mu m^2$ of the two samples were measured by AFM. In order to obtain reliable data, we randomly chose five areas to be measured and the average values are listed in Table 1. Generally, the film surfaces of the two samples are fairly smooth, and sample 1 is obviously better than sample 2 in roughness. For convenience, we simply define a dispersion factor as

$$Q = 2\frac{q_2 - q_1}{q_2 + q_1} \tag{1}$$

to quantify the difference in roughness between the two samples, where q_i ($i = 1, 2$) is the roughness. Evidently, the difference in Q between the two samples is rather large for YSZ thin films, and the dispersion is close to 50% for either R_q or A_v. In contrast, the difference is smaller for YBCO thin films, which is only

about 10% for both. Therefore, the AFM survey indicates that the pretreating method of SOI substrates more affects the crystal quality of YSZ thin film, which is accordant with the conclusion deduced from ω-scan.

Table 1. Comparison of surface roughness between two samples (1 Å = 0.1 nm).

	YSZ		YBCO	
	R_q/Å	A_v/Å	R_q/Å	A_v/Å
Sample 1	29.08	21.06	71.76	56.90
Sample 2	45.84	37.78	79.62	62.82
Dispersion/%	44.7	56.8	10.4	9.9

Figure 3 shows the curves for the values of normalized resistance $R(T)/R$ (290 K) versus temperature of the YBCO thin films (≈200 nm) in the two samples. It is clear that the two curves are almost the same. They have an identical slope in the normal state and a similar zero resistance temperature (≈88 K). The inset is the magnification of the two curves around the transition temperature. There is only a very slight difference in transition width between the two samples, which may probably be attributed to the inaccurate duplication of the film growth conditions during the PLD process.

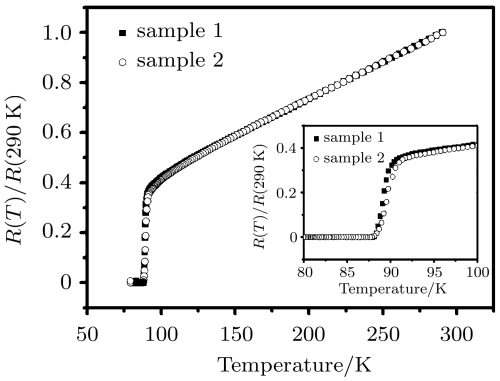


Fig.3. Curves for normalized resistance $R(T)/R$ (290 K) versus temperature for about 200-nm-thick YBCO thin films of the two samples.

The surface morphology and cracks of the YBCO thin films (≈70 nm) were investigated by SEM as shown in Fig.4. The left panels, (a) and (c), are for sample 1, and the right panels, (b) and (d), are for sample 2. A remarkably higher density of pinholes occurs in the surface of sample 2. As reported by Cima *et al*, Ba element in YBCO can react with YSZ at high temperatures and form a stable product $BaZrO_3$ (BZO). Generally, a 2–3 nm thick dense BZO layer can effectively stop further interface interactions, and thus ensuring a high quality YBCO thin film on the top.[17] However, the presence of corrosion steps on the substrate surface makes anti-phase boundaries easily formed in YSZ and YBCO layers, where the chemical diffusion is enhanced and the interaction continues. In short, HF pretreatment induced corrosion steps lead to poorer crystallinity and rougher surface of YSZ films, and thus more chemical diffusion and finally the appearance of a higher density of pinholes in the YBCO layer. Meanwhile, Si element diffusion from the substrate into the YBCO layer through the anti-phase boundaries can also result in pinholes.

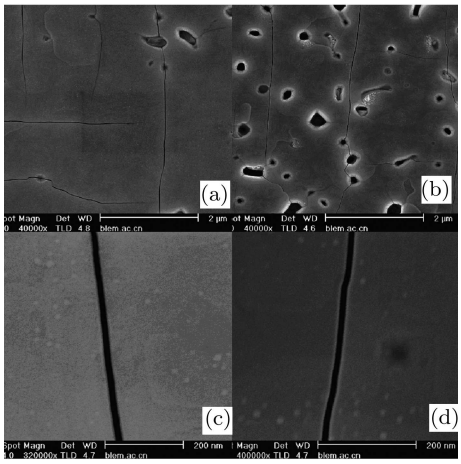


Fig.4. SEM images of YBCO thin films for samples 1(a) and 1(c), and samples 2(b) and 2(d), where a higher density of pinholes appears in films deposited on SOI substrates with HF pretreatment (sample 2) and the average crack spacing and crack width for the two samples are almost the same.

In addition, although the SOI substrate is considered more compliant than Si due to the buried polycrystalline oxide layer, the stress resulting from the very large thermal coefficient mismatch between the film and the substrate cannot be effectively relaxed, probably because of the relatively large thickness of the top silicon layer (≈200 nm) in this experiment. The strain in the heterostructure is then predominantly accommodated by the epilayer. As the YBCO film thickness is higher than several tens of nanometres, microcracks propagate along the [100] and [010] directions of YBCO, thus drastically reducing T_C and J_C, and bringing about a strong aging effect. We carefully measured and calculated the average crack

spacings in the two samples, which are almost the same, about 1.5 μm. As proposed by Olsson *et al*,[18] films with identical thicknesses should result in identical average crack spacings. This could well explain the above results. Moreover, as shown in Figs.4(c) and 4(d), the crack widths are about 20 and 14 nm for samples 1 and 2, respectively. We reported that the crack width was also determined by the thickness of YBCO film.[19] Therefore, the difference in crack width observed here is attributed mainly to the random sampling of cracks rather than to the pretreating method of the SOI substrates.

4. Conclusion

We have successfully deposited YSZ and YBCO bilayer films on SOI substrates with and without the native amorphous SiO_2 layer by using the PLD method. A detailed comparison shows that the quality of sample 1 is better than that of sample 2, especially for YSZ thin films. Therefore, we assure that preserving the native amorphous SiO_2 layer can not only simplify the experimental process but also obtain higher quality YSZ and YBCO thin films.

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