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Growth of YBaCuO Films on Si(100) Substrates with Ultrathin Metal Overlayers

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YBaCuO superconductor films were grown on Si(100) substrates with Ba ultrathin overlayers by molecular beam epitaxy method with NO_2 gas. Ba ultrathin layers were deposited on clean Si(100) at substrate temperature Ts of 860 ℃, and showed 2× 1 structure. Ultrathin SiO_x layers were formed in Ba/Si after the heat treatment at 200 ℃ in an NO_2 atmosphere followed by the heat treatment at 690℃ in a vacuum. It was found by X-ray photoelectron spectroscopy that the Ba layers are on the top of the sample.

1. INTRODUCTION

For the formation of oxide superconductor films on semiconductors or superconductor/ semiconductor junctions, semiconductors such as Si and GaP may be useful due to the good coincidence in lattice constant. However, Si easily reacts with oxygen and the compositional metal films thicker than a few monolayers(ML)[1] (1ML means the number of atoms on Si(100) surface.). On the other hand, ultrathin metal overlayer with an ordered structure has a possibility of avoiding the direct reaction between Si and the compositional elements[2]. Thus, it is important to investigate the reaction between Si and the metal overlayers in an oxidizing atmosphere or under a real growth condition of the oxide. In this paper, we report the oxidation of Si(100) with ultrathin metal overlayers and the growth of YBaCuO films on these systems by molecular beam epitaxy(MBE) method.

2. EXPERIMENTAL

An ultrahigh-vacuum (UHV) system composed of two chambers and a transport chamber was used in this experiment. The schematic diagram of the system is shown in Fig.1. The right chamber was used for the cleaning of Si substrates and for the growth of Ba layers, and the left chamber was used for the oxidation of the sample and the growth of YBaCuO films. The total base pressures of the right and left chambers were below 2 and 6 $\times 10^{-10}$ Torr, respectively. We used nitric dioxide(NO_2) gas as a strong oxidant[3,4]. Studies

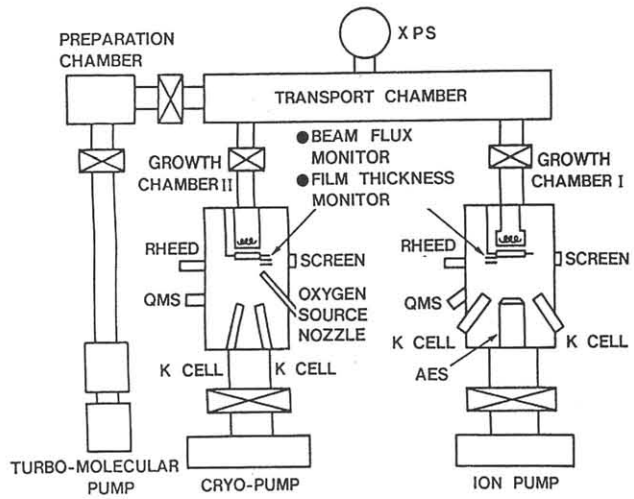

Fig.1 Schematic diagram of ultrahigh vacuum system used for YBaCuO films on Si.

of the adsorbed atoms and the chemical bond between the elements, were performed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Surface structures were studied by reflection high energy electron diffraction(RHEED).

Si(100)± 0.2° ,± 1° substrates with a resistivity of 0.01～0.06 Ω cm were used in the experiments, and were cleaned at a substrate temperature T_S of 860℃ in a vacuum by a method[5]. About 1 ML Ba was deposited on the substrate at T_S of 860℃ with impinging atoms of 6.9×10^{11} 1/cm^{2}s. After cooling the sample down to 200℃, 1ML thick Ba was further deposited on the sample. The sample was oxidized for 30 seconds in NO_2 atmosphere

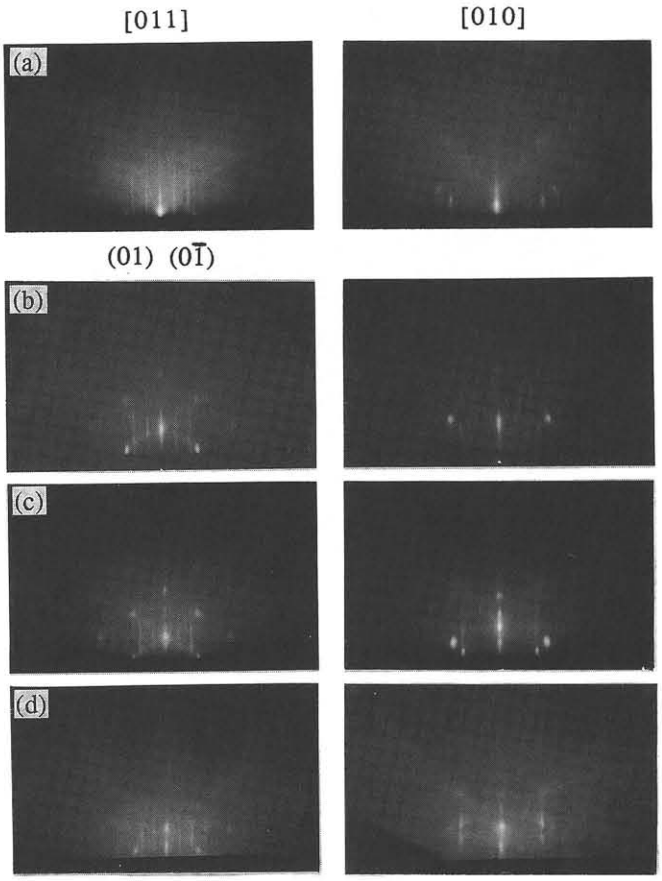

Fig.2 RHEED patterns for Si(100) surface after cleaning (a), with ~1 ML Ba overlayer (b), ~ 2 ML Ba overlayer (c) and Cu/2ML Ba overlayers (d). Right and left photographs show the patterns observed in the [010] and [011] directions, respectively.

with a pressure of 5×10^{-7} Torr, and was successively heated for 8 minutes at 690℃, and was finally exposed to Cu beam with a quantity of 1ML. XPS, AES and RHEED measurements were done on each step.

3000 Å thick YBaCuO films were grown at T_S of 690℃ by MBE with NO_2 gas on Si(100) with 1.4 ML thick Ba overlayers which adsorbed some oxygen. We used pure metals in Knudsen cells and 0.8 Å /s as a growth rate. Impinging molecules of NO_2 on the substrate was about 6×10^{16} 1/cm^{2}s and the pressure was about 10^{-5}Torr at the background. The quality of the film was evaluated by X-ray diffraction pattern and the resistivity versus temperature characteristics was measured. After forming ohmic contacts of YBaCuO and n-type Si with Au and Au-Sb, respectively, the current-voltage characteristics was also measured. The interface between YBaCuO film and Si was observed by transmission electron microscope (TEM).

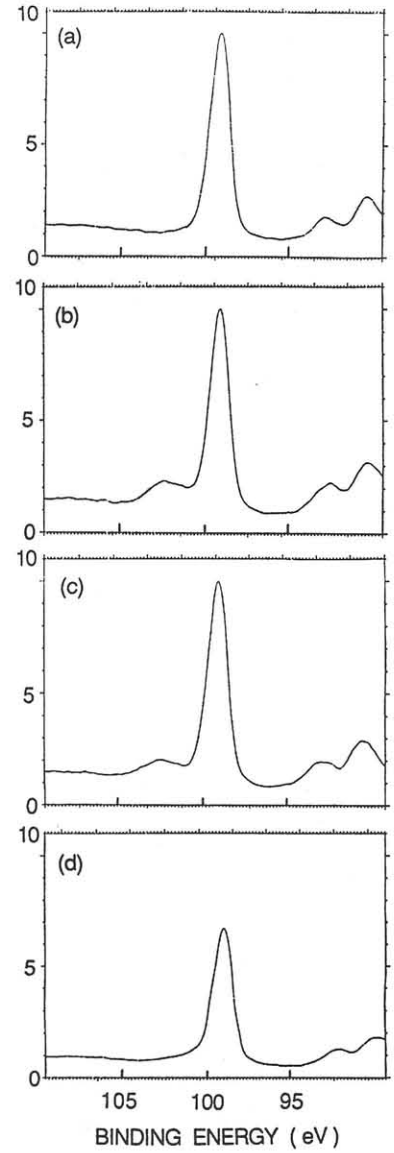

Fig.3 XPS Si2p signals for ~2ML Ba/Si(100) (a), ~2ML Ba/Si heat-treated at 200℃ in NO_2 atmosphere (b), ~2ML Ba/Si heat-treated at 690℃ in vacuum (c) and Cu/Ba/Si (d).

3. RESULTS AND DISCUSSION

Figure 2 shows RHEED patterns for Si(100) after the cleaning (a), the deposition of ~1ML Ba at 860 ℃ (b), the further deposition of ~1ML Ba at 200℃ (c) and the deposition of 1 ML Cu (d). The patterns on every step suggested the existence of 2× 1 structures. However, the streak lines characteristic to the structure became dim after the exposure to NO_2 gas and the succeeding heat treatment at 690 ℃. The structures were not obtained for the deposition of Ba source which adsorbed some oxygen.

In order to study the diffusion of Ba atoms into Si, XPS measurements for several detection angles were done for 1ML Ba/Si system. As an angle θ between the sample surface and the

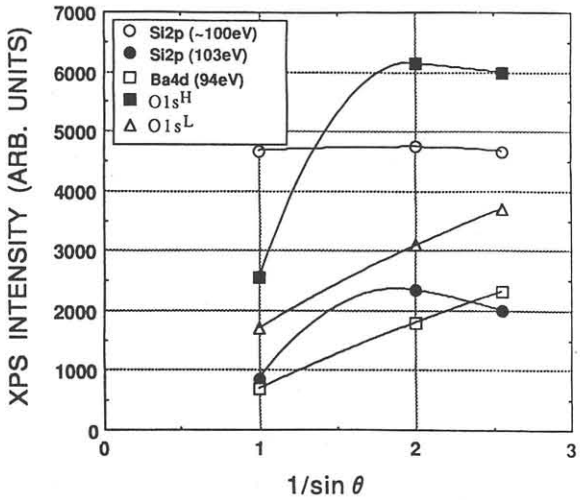

Fig.4 XPS intensities of Ba4d, O1s, Si2p(100eV) and Si2p(103eV) as a function of $1/\sin\theta$. $O1s^H$ and $O1s^L$ mean two O1s signals into which O1s signals are divided on high and low binding energy sides.

detection direction decreased, the intensity for Ba4d signal increased and the intensity for Si2p decreased to the contrary. Similar result was obtained for Si(100) with Ba overlayers which adsorbed some oxygen.

The weak oxidation of Si by NO_2 was detected by XPS , as shown in Fig.3. After the exposure of Ba/Si to NO_2, a weak peak peculiar to SiO_x was generated on the higher binding energy side (100～104eV) of a peak of Si2p(～100eV)(b). The peak intensity decreased after the heating at 690 ℃ . The thickness of the SiO_x layer was estimated to be 3～4Å from the ratio between Si2p(～103eV) and Si2p(～100eV) intensities..

Figure 4 shows Ba4d(94eV), Si2p(100eV), Si2p(103eV) and O1s XPS intensities for 2ML Ba/Si heat-treated at 690 ℃ as a function of $1/\sin\theta$. $O1s^H$ and $O1s^L$ show the intensities of two O1s signals into which O1s signals were divided on the high and low binding energy sides. Good correspondence was obtained between the changes of Ba4d and $O1s^L$ intensities or the changes of Si2p(103eV) and $O1s^H$ intensities. The increase in Ba4d intensity with increasing $1/\sin\theta$ and the decrease in Si2p(103eV) in higher $1/\sin\theta$ suggested that the Ba layers are on the top of the sample.

Surprisingly, the SiO_x layer was reduced by the irradiation of Cu beam, as shown in Fig.3(d). Since Cu atoms were not detected on the sample and the decrease in O1s intensity was found by XPS, it was thought that Cu atoms desorb with oxygen.

It was found by XRD patterns that c-axis of YBaCuO thin films on Ba/Si(100) is perpendicular to Si(100) surface. The critical temperature of the film was about 30K. Figure5 shows a cross-sectional TEM image of the interface between YBaCuO film and Si. An

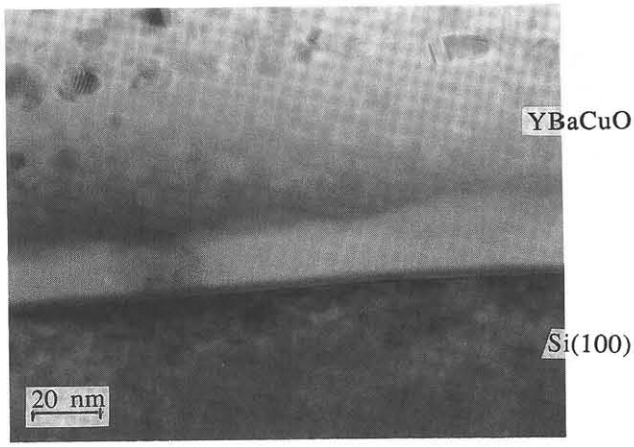

Fig.5 Cross-sectional TEM image of the interface between YBaCuO film and Ba/Si(100).

amorphous layer with a thickness of about 200 Å was observed at the interface. The current-voltage characteristics was measured for this sample. A nonlinear and asymmetric feature was obtained.

4. CONCLUSIONS

An ordered structure of Ba atoms was formed on Si(100) by the deposition at a temperature of 860 ℃. The succeeding heat treatment in an NO_2 atmosphere generated an ultrathin SiO_x layer. This SiO_x layer was reduced by the irradiation of Cu beam. YBaCuO superconductor films were successfully grown on Si(100) with an ultrathin Ba overlayer by MBE with NO_2 gas. The current-voltage characteristics was obtained for this sample.

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