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Formation of Y-Ba-Cu-O Superconducting Thin Films on Semiconductor Substrates

Michihiro MIYAUCHI, Koichi MIZUNO, Takeshi KAMADA,
Kentaro SETSUNE, Takashi HIRAO and Kiyotaka WASA
Central Research Laboratories,
Matsushita Electric Industrial Co., Ltd.,
3-15, Yagumonakamachi, Moriguchi, Osaka 570, Japan

We prepared the superconducting Y-Ba-Cu-O thin films on Si, CaF_2/Si and CaF_2/GaAs substrates at the substrate temperatures below 600°C by rf planar magnetron sputtering. The onset temperatures of films on Si, CaF_2/Si and CaF_2/GaAs were 81K, 82K and 75K, respectively. The zero resistance temperatures of films on Si, CaF_2/Si and CaF_2/GaAs were achieved below 29K, 56K and 45K, respectively.

1. Introduction

Since the discovery of high T_c oxide superconductor, many efforts have been done to prepare these materials in the form of thin films on suitable substrates for the fundamental physics studies and the purpose of various applications. One of the problems of fabrication for oxide superconducting thin films is the selection of substrates. Considering the applications to electronic devices, it is very important to form the superconducting thin films on semiconductors such as Si and GaAs But, for Y-Ba-Cu-O system, crystallized thin films were prepared on a substrate heated up to 700°C or by a post-annealing treatment above 850°C. In these cases, Ba elements of Y-Ba-Cu-O films prepared on Si substrate combine with Si elements and diffuse into heated Si substrate easily[1]. Moreover, the difference of a thermal expansion coefficient between these new materials and substrates results in the generation of cracks in the thin films. Thus, low temperature processes are indispensable to form superconducting thin films on the substrate integrated by semiconductor devices and interconnection.

On the other hand, considering the electronic devices, superconducting thin films should be also prepared on insulator/ semiconductor structure. To obtain the crystallized superconducting thin films, substrates should be used in the form of wafers having crystalline surface. The crystalline thin films such as ZrO_2, CaF_2, BaF_2, SrF_2, SrO, MgO and etc. have been grown epitaxially on Si substrates in the form of SOI(Si on Insulator)[2].

In this paper, we examined the fabrication of superconducting thin films on semiconductors such as Si and GaAs. We prepared the superconducting and insulating films at temperatures lower than 600°C in an attempt to fabricate hybrid devices of semiconductors and superconductors.

2. Low-temperature Process

The structural analyses for Y-Ba-Cu-O ceramics have suggested that the structural transition from the nonsuperconducting tetragonal phase into superconducting orthorhombic phase occurs around 600 -

$700^{\circ}C$[3]. If the substrate temperature during the deposition T_S satisfies the following relation

$$T_e < T_s < T_t \quad (1)$$

where T_e denotes the epitaxial temperature and T_t, the transition temperature from the tetragonal to the orthorhombic phase, the as-sputtered films show the single crystal phase.

Thin film processes are classified into three processes: (1) deposition at a low substrate temperature followed by a post-annealing at around $900^{\circ}C$; (2) deposition at a crystallizing temperature of 600 - $700^{\circ}C$ followed by the post-annealing; (3) deposition at a crystallizing temperature under oxidizing atmosphere. In the process (2) and (3), as-sputtered films are crystallized. It is suggested that crystallized Y-Ba-Cu-O ceramics are able to be oxidized by annealing at the temperature lower than $450^{\circ}C$. So the control of oxygen vacancies will be attained at lower temperature when the vacancy control is conducted by low temperature post-annealing in oxygen atmosphere or by an oxygen ion bombardment on the film surface during the film growth.

3. Buffer layer

For the deposition of crystalline Y-Ba-Cu-O thin films, substrates should be selected. The crystallographic properties of the crystal substrates which we can select for the growth of Y-Ba-Cu-O are listed in Table 1.

To prepare the superconducting thin film on Si and GaAs, we chose CaF_2 for a buffer layer. The reasons for the choice of this kind of buffer layer are follows. (1) CaF_2 crystal has a cubic structure which is similar to those of popular semiconductors such as Si, GaAs and GaP. The lattice mismatch between CaF_2 and Si is very

Table 1 Substrates for the epitaxial growth of high T_c superconductors

	Crystal System	Lattice Constants	Thermal Expansion Coefficient
$YBa_2Cu_3O_x$	orthorhombic	a=3.82A b=3.89A c=11.68A	$10\text{-}15\times10^{-6}$/K
sapphire	trigonal	hex. axes a'=4.76A c'=13.00A	//c: 8×10^{-6}/K ⊥c: 7.5×10^{-6}/K
MgO	cubic	a=4.20A	13.8×10^{-6}/K
YSZ	cubic	a=5.16A	10×10^{-6}/K
$SrTiO_3$	cubic	a=3.91A	10.8×10^{-6}/K
Si	cubic	a=5.43A	2.4×10^{-6}/K
GaAs	cubic	a=5.65A	5.8×10^{-6}/K
CaF_2	cubic	a=5.46A	19×10^{-6}/K
SrF_2	cubic	a=5.80A	18×10^{-6}/K
BaF_2	cubic	a=6.20A	18×10^{-6}/K

small(0.6% at room temperature). Therefore the epitaxial growth of CaF_2 film on Si substrate is obtained easily. (2) The single crystal CaF_2 film on Si is obtained at the substrate temperature of $600^{\circ}C$ during the growth[2]. (3) As the lattice constant of CaF_2 can be changed by mixing Sr or Ba element, this buffer layer can be applied easily to other semiconductors. Moreover we consider that Y-Ba-Cu-O superconducting thin film may be epitaxially grown on CaF_2 since matching between (110) Y-Ba-Cu-O and (001) CaF_2 lattice constant is good.

4. Experimental Procedure

The substrates used in this work were (001) oriented single crystal Si and GaAs wafers. These were chemically cleaned and set in an evaporation chamber. The 200nm thick CaF_2 films were evaporated from CaF_2 powder with 99.99% purity using Ta crucible. The pressure during the deposition was lower than 4×10^{-7}Torr. The substrate temperature of Si and GaAs during the deposition was kept at

$600^{o}C$ and was measured using a two-wavelength infrared radiation thermometer.

Oxide superconducting thin films were prepared by rf planar magnetron sputtering. The target was made by sintering the mixture of Y_2O_3, $BaCO_3$, and CuO in air at $900^{o}C$ for 8h. The compositional ratio of Y-Ba-Cu was 1-2-4.5. The sputtering was carried out under the conditions listed in Table 2. A mixture of Ar and O_2 was used for sputtering gas. After deposition, substrate was cooled to $400^{o}C$ for 30min in oxygen atmosphere and then heater current was turned off.

5. Results and Discussion

5-1 Superconducting Thin Films on CaF_2/Si

The crystallinity of CaF_2 on Si(001) substrate was clarified by X-ray diffraction and electron diffraction(RHEED). Generally, F elements in CaF_2 film are decomposed easily by irradiation of energy beam. So, we could get only blurry spot pattern of RHHED. On the other hand, high peak of (004) and weak peaks of (220) , (311) and (111) were observed in X-ray diffraction pattern of CaF_2 film. We consider that the CaF_2 film didn't grow epitaxially on Si because the silicon oxide and impurities could not be removed perfectly from silicon surface by the low heating temperature as $600^{o}C$.

Figure 1 shows the x-ray diffraction patterns of Y-Ba-Cu-O films on CaF_2/Si(001) made with various gas ratio of Ar and O_2. The (00n) (n=1,2,3,5,6) peaks of superconducting phase of Y-Ba-Cu-O were observed. It shows that the Y-Ba-Cu-O films on CaF_2/Si(001) were primarily single phase and c axis is oriented

Table 2 Sputtering conditions of Y-Ba-Cu-O films.

Substrate	CaF_2/Si(001),	CaF_2/GaAs(001),	Si(001)
Substrate temperature	$600^{o}C$	$450^{o}C$	$600^{o}C$
Gas pressure	2Pa	0.4Pa	0.4Pa
Target	$Y_1Ba_2Cu_{4.5}O_x$		
Sputtering gas	$Ar+O_2$		
rf input power	130-150W		
Growth rate	8nm/min		

lattice parameter of Y-Ba-Cu-O films is c=11.72A. However the peak intensities of Y-Ba-Cu-O films on CaF_2/Si(001) are smaller than those of Y-Ba-Cu-O films on MgO and $SrTiO_3$.

Figure 2 shows the temperature dependence of resistivity For the sputtering gas with 1-1 ratio of Ar-O_2, the onset temperature was 82K and zero resistance was achieved below 56K. The critical current density at 4.2K was about $1x10^4 A/cm^2$.

5-2 Superconducting Films on CaF_2/GaAs(001)

The X-ray diffraction pattern for CaF_2 film on GaAs(001) substrate is shown in Fig.3. The (004) peak of CaF_2 film strongly appeared and the (022) peak was weakly

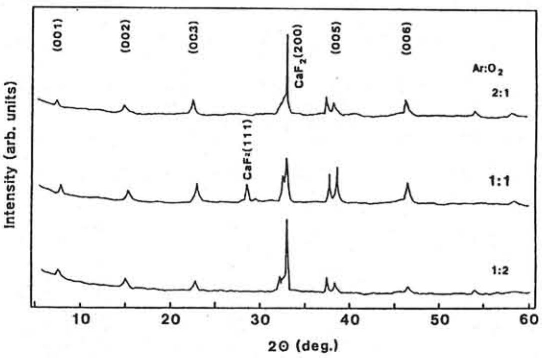

Fig. 1 X-ray diffraction patterns of Y-Ba-Cu-O films on CaF_2/Si(001) made with various gas ratio of Ar and O_2.

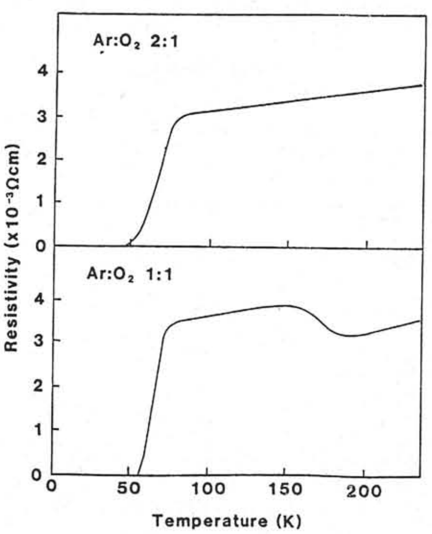

Fig. 2 Temperature dependence of resistivity of Y-Ba-Cu-O films on CaF_2/Si(001).

observed.

The properties of superconducting films strongly depend on substrate temperature during the deposition. In the case of substrate temperature above $500^{\circ}C$, the Y-Ba-Cu-O films peeled off from $CaF_2/GaAs$ substrates. So the deposition was curried out at the temperature of $450^{\circ}C$. The onset temperature of prepared Y-Ba-Cu-O film was 75K and zero resistance temperature was 45K as shown in Fig.4. The critical current density at 4.2K was estimated to be $2x10^3 A/cm^2$. X-ray diffraction data showed only one peak at $2\theta=44^{\circ}$.

5-3 Superconducting Films on Si(001)

Figure 5 shows the resistive transition of the Y-Ba-Cu-O film prepared directly on the (001) single crystal Si substrate at the substrate temperature of $600^{\circ}C$ during the deposition. The onset temperature was 81K and zero resistance

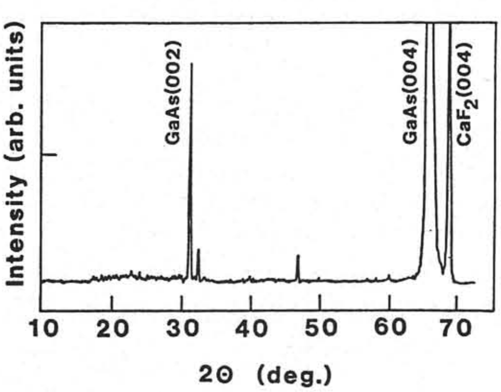

Fig.3 X-ray diffraction pattern of CaF_2 film on GaAs(001).

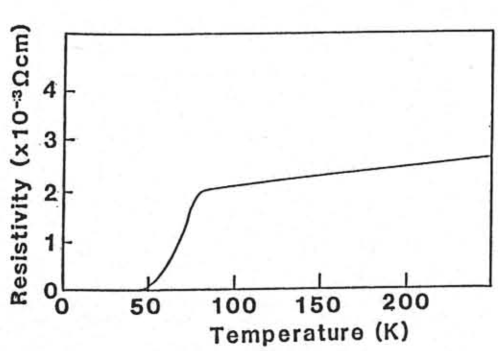

Fig. 4 Temperature dependence of resistivity of Y-Ba-Cu-O film on CaF_2/GaAs(001).

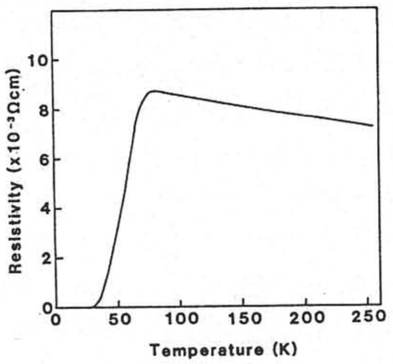

Fig. 5 Temperature dependence of resistivity of Y-Ba-Cu-O film on Si(001).

temperature was 29K. The critical current density at 4.2K was $1.5x10^3 A/cm^2$. The Y-Ba-Cu-O film was preferentially oriented to c-axis. It is considered that this superconductivity was obtained since the interaction between the superconducting thin film and Si substrate may be reduced in case of our low temperature process.

6. Summary

We tried to prepare the Y-Ba-Cu-O superconducting thin films on Si, CaF_2/Si and $CaF_2/GaAs$ substrates at the substrate temperatures below $600^{\circ}C$. Although the single crystal thin films of Y-Ba-Cu-O superconductor and CaF_2 could not be obtained on Si and GaAs substrates, we succeeded in getting the superconducting properties on Si and GaAs substrates using the low-temperature(below $600^{\circ}C$) processes. We consider that superconducting properties of these films can be improved by optimizing process conditions.

Acknowledgement

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