

Growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Films on Si with Al_2O_3 Buffer Layer and on LiNbO_3 by *In-situ* Metalorganic Chemical Vapor Deposition?

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We present deposition of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films on Si (100) substrate with an Al_2O_3 buffer layer and LiNbO_3 single crystal substrates by metalorganic chemical vapor deposition. Organometallic sources of β -diketonate complexes of $\text{Y}(\text{dpm})_3$, $\text{Ba}(\text{dpm})_2$, $\text{Cu}(\text{dpm})_2$, and aluminum isopropoxide were **used** as yttrium, barium, copper, and aluminum precursors, respectively. A resistive heated vertical cold-wall reaction chamber using N_2O gas as an oxidizer was successful for depositing thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and an epitaxial Al_2O_3 buffer layer without post annealing. A buffer layer of MOCVD grown Al_2O_3 film on silicon (100) was found to be a γ phase Al_2O_3 hetero-epitaxial film from the X-ray diffraction analysis. An As-deposited film on $\text{Al}_2\text{O}_3/\text{Si}(100)$ substrate at a substrate temperature of $800 \sim 850^\circ \text{C}$ showed superconducting behavior at $T_{c,zero} = 52 \text{ K}$. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}/\text{Al}_2\text{O}_3/\text{Si}(100)$, the Al_2O_3 hetero-epitaxial buffer layer is a diffusion barrier between the superconducting film and the silicon substrate during high temperature growth. We also discuss *in-situ* MOCVD growth of an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin film on a z-cut LiNbO_3 single crystalline substrate showing $T_{c,zero} = 85 \text{ K}$. *In-situ* formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films on lattice mismatched LiNbO_3 substrate is useful for future integrated optical device applications.

High T_c superconductors of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBaCuO) have strong potential for future device applications depending on thin film fabrication with desirable properties. It is necessary to prepare *in-situ* film deposition without requiring high-temperature post-annealing. Popular substrates for YBaCuO thin film deposition by a variety of techniques are SrTiO_3 , MgO , and yttria stabilized zirconia (YSZ). Recently, successful preparations of YBaCuO thin films onto various substrates such as LaAlO_3 ,¹⁻³ LaGaO_3 ,⁴⁻⁵ NdGaO_3 ,⁴ YbFeO_3 ,⁶ Al_2O_3 ⁷⁻⁹ and LiNbO_3 ¹⁰⁻¹² have been reported. These single crystalline substrates are usually expensive and fragile. It is desirable to deposit the YBaCuO films directly onto silicon substrates. The silicon substrates are popular and compatible with the current electronics industry. Although there is

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some progress on direct deposition of the films on silicon, severe chemical reaction at the interface is not avoidable. Buffer layers are usually introduced between Si and YBaCuO to prevent interdiffusion during the high temperature processing. Insulating materials for the buffer layer such as SiO_2 ,¹³ ZrO_2 ,¹⁴ MgO ,¹⁵ and BaTiO_3 ¹⁶ were reported. A conducting metallic oxide of RuO_2 was also used as a buffer layer.¹⁷ Most of the buffer layer was fabricated by physical vapor deposition. It is of interest to process the buffer and YBaCuO layer by chemical vapor deposition because of compatibility with current semiconductor technology. LiNbO_3 substrates have become, perhaps, the most common material used in integrated optical devices because of excellent nonlinear and electro-optical properties. There were reports on epitaxial growth of the film by *in-situ* laser ablation¹⁸ and dc magnetron sputtering.¹⁹

In this proceeding we report deposition of superconducting YBaCuO thin films on LiNbO_3 and Si substrates, by metalorganic chemical vapor deposition (MOCVD). The buffer layer of Al_2O_3 was grown on (100) Si followed by *in-situ* MOCVD deposition of YBaCuO. A heteroepitaxially grown γ - Al_2O_3 buffer layer exhibited a good diffusion barrier property in YBaCuO/ Al_2O_3 /Si. As-deposited films on a z-cut LiNbO_3 single crystalline substrate became superconducting with polycrystalline behavior. Our results suggested that these films did not have a sharp interface.

We used β -diketonate complexes of $\text{Y}(\text{dpm})_3$, $\text{Ba}(\text{dpm})_2$, $\text{Cu}(\text{dpm})_2$, where dpm = dipivalolmethanate, and aluminum isopropoxide [$\text{Al}(\text{OC}_3\text{H}_7)_3$] as yttrium, barium, copper, and aluminum precursors, respectively. Source containers were immersed in constant temperature controlled oil baths at 126, 114, 250, and 100 °C for Y, Ba, Cu, and Al precursors, respectively. Connecting tubes between the source bath and growth chamber maintained it at 250 °C to prevent condensation of the organometallic source during transport. Substrates of (100) Si, SrTiO_3 , z-cut LiNbO_3 , and YSZ were loaded into a resistively heated susceptor of the vertical cold-wall type reaction chamber. Deposition temperature was 800 ~ 850 °C measured at the surface close to the substrate. N_2O gas at flow rate of 100 sccm was separately supplied into the growth chamber at total pressure of 10 torr for *in-situ* growth. Flowing rates of argon carrier gas were 10, 35, 15, and 30 sccm for Y, Ba, Cu, and Al precursors, respectively. Typical deposition time was 180 minutes followed by annealing at 500 °C for two hours under an oxygen atmosphere and slow cooling down to room temperature at a rate of 5 °C/minute. In order to minimize the problem of vapor pressure reduction¹⁸ caused by gradual decomposition of the barium precursor, a fresh new source was charged for every experimental run. We measured the resistance dependence of the temperature (R-T) by a conventional four-point dc measurement using a closed cycle helium refrigerator. Compositional analysis was carried out by inductive coupled plasma analysis (ICP), wavelength dispersive spectroscopy (WDS), and Auger electron spectroscopy (AES). We used X-ray diffraction (XRD) and scanning electron microscopy (SEM) to study structural properties.

Composition of the films can be varied either by adjusting the argon carrier gas flowing

rates of each precursor or by changing the bath temperature. In order to obtain stoichiometry of 1-2-3, we varied the temperature of the oil bath for the precursor while fixing the flow rates mentioned above. Figure 1 shows the R-T curves of the films from several experimental runs for various oil bath temperatures. Table I shows compositional analysis by WDS and also by ICP (not shown). We adjusted the oil bath temperatures such that the relative compositional ratio of the film is close to that of the bulk value with higher T. The most favorable oil bath temperatures were 126, 114, and 250 °C for Y, Ba, and Cu respectively. The YBaCuO films grown at a substrate temperature of 800 °C using N₂O gas showed superconducting behavior without post annealing. In figure 2, the R-T curves of the thin films on SrTiO₃ and z-cut LiNbO₃ substrate show an onset temperature at 91 K and T_{c,zero} = 80 K and 83 K, respectively. Thickness of the film was less than 1 μm. Figure 3 (B) shows SEM of the surface of YBaCuO/LiNbO₃. Polycrystalline behavior with random orientation was also confirmed by XRD (figure 6). A Laue back reflection pattern was taken to confirm the surface orientation of z-cut LiNbO₃. We attempted the deposition onto y-cut LiNbO₃, but failed to obtain superconducting films. The report¹⁰ on epitaxial growth of the thin films on y-cut LiNbO₃ substrates by laser ablation discussed two main problems. First, Li atoms diffuse out to the surface during the high temperature processing presumably because they are light. Second, a poor lattice match between the two materials. LiNbO₃ has trigonal symmetry¹⁹ while YBaCuO has a rectangular arrangement. Polycrystalline film seems to be unavoidable because of the large lattice mismatch and high deposition tempera-

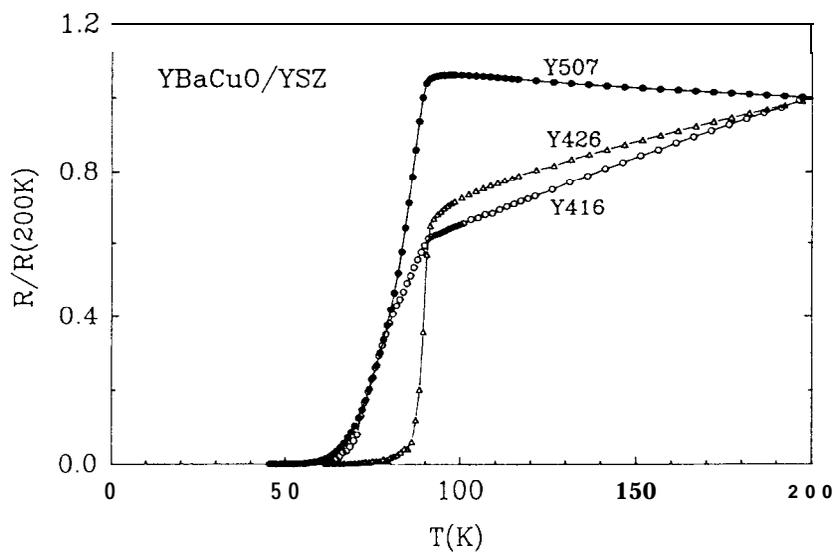


FIG. 1. R-T curves of the YBaCuO thin films on YSZ for various experimental conditions. Compositional variations by WDS are listed in Table I.

TABLE I. Semi-quantitative analysis of compositional ratios for the films by wavelength dispersive spectroscopy (WDS) and oil bath temperatures of precursors

SAMPLE NAME	SUBSTRATE	Y	Ba	CU	O	T_c
STANDARD	<< BULK >>	1	3.05	3.00	4.07	90 K
Y416	YSZ	1	1.34	2.70	3.69	64 K
Y426	YSZ	1	2.09	2.81	4.31	80 K
Y503	YSZ	1	1.16	4.49	6.65	30 K
Y507	YSZ	1	0.76	4.01	6.94	60 K
YS426	Si	1	1.75	3.30	12.21	

SAMPLE NAME	OIL BATH TEMPERATURE ($^{\circ}\text{C}$)		
	Y(dpm) ₃	Ba(dpm) ₂	Cu(dpm) ₂
Y416	126	240	114
Y426	126	250	114
Y503	136	250	124
Y507	136	240	124
YS426	126	250	114

ture at 800 $^{\circ}\text{C}$. However, use of N_2O gas stimulated the supply of ionized oxygen during the growth process for *in-situ* MOCVD. Figure 4 (B) shows the AES spectrum of the surface of $\text{YBaCuO}/\text{LiNbO}_3$. Relative intensity ratios of peaks for Y, Ba, Cu, and O are similar to those of $\text{YBaCuO}/\text{SrTiO}_3$. There is no significant residual carbon participation. An earlier report¹¹ showed that the interface between YBaCuO and LiNbO_3 is not sharp from the AES depth profile results. We observed a Ba-rich interface layer as well as out-diffusion of Li and Nb from the substrate.

A buffer layer of Al_2O_3 film on (100) Si was grown by MOCVD using aluminum isopropoxide and N_2O at a substrate temperature of 740 $^{\circ}\text{C}$. XRD analysis suggested that a buffer layer of Al_2O_3 film on (100) Si is found to be a γ phase hetero-epitaxial film which is the subject of a separate publication.¹² Possible lattice matching relationships are (100) $\gamma\text{-Al}_2\text{O}_3//\text{Si}$ (100) and (100) $\gamma\text{-Al}_2\text{O}_3//\text{Si}$ (110). The stoichiometry of as-grown Al_2O_3 film was found to be similar to that of sapphire observed from AES. Room temperature capacitance-voltage measurements showed clearly metal-insulator-semiconductor behaviors for samples with the Al_2O_3 insulator gate. Thickness of the film was 2200 \AA determined from capacitance-voltage measurement. After characterization of $\text{Al}_2\text{O}_3/\text{Si}$, the substrate with the buffer layer was loaded

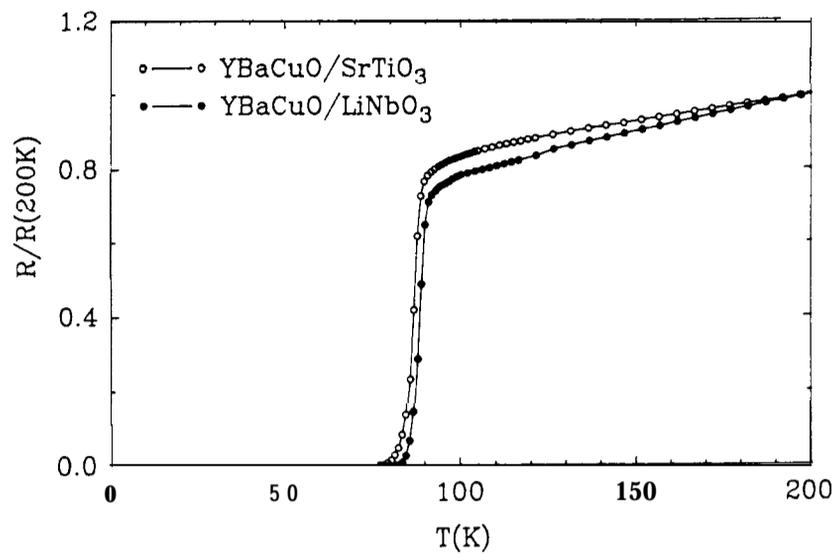


FIG. 2. R-T curves of *in-situ* MOCVD grown YBaCuO thin films on SrTiO₃ and LiNbO₃.

again into the growth chamber followed by deposition of YBaCuO at 800 °C for 180 minutes. SEM of the surface of YBaCuO/Al₂O₃/Si is shown in figure 3 (A). It is a polycrystalline thin film. There was no preferred orientation indicating no obvious (001) peaks in XRD. The polycrystalline property of the film might be caused by a chemical reaction or strains at the film-substrate interface. Figure 5 shows the R-T curve of an *in-situ* MOCVD grown YBCO thin film on Al₂O₃/Si with $T_{c,zero} = 52$ K. The film has semiconducting behavior above T_c with a broad transition tail. The AES result in figure 4 (A) reveals that stoichiometry is close to that of the

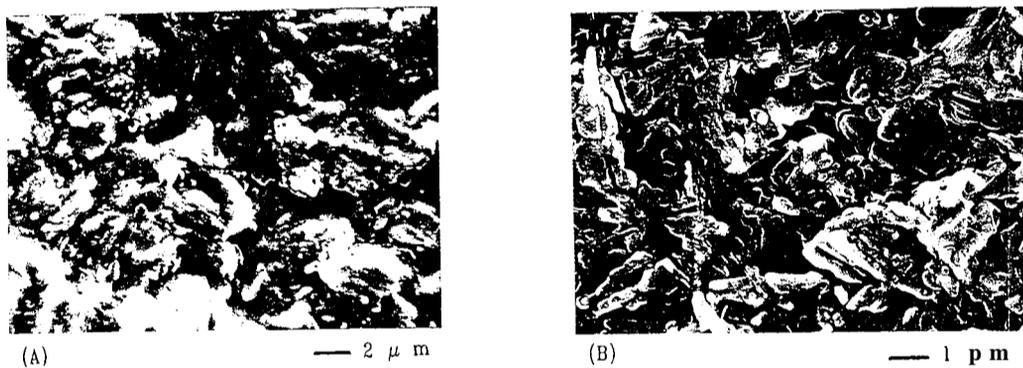


FIG. 3. (A) SEM photographs of YBaCuO/Al₂O₃/Si(100). (B) SEM photographs of YBaCuO/LiNbO₃.

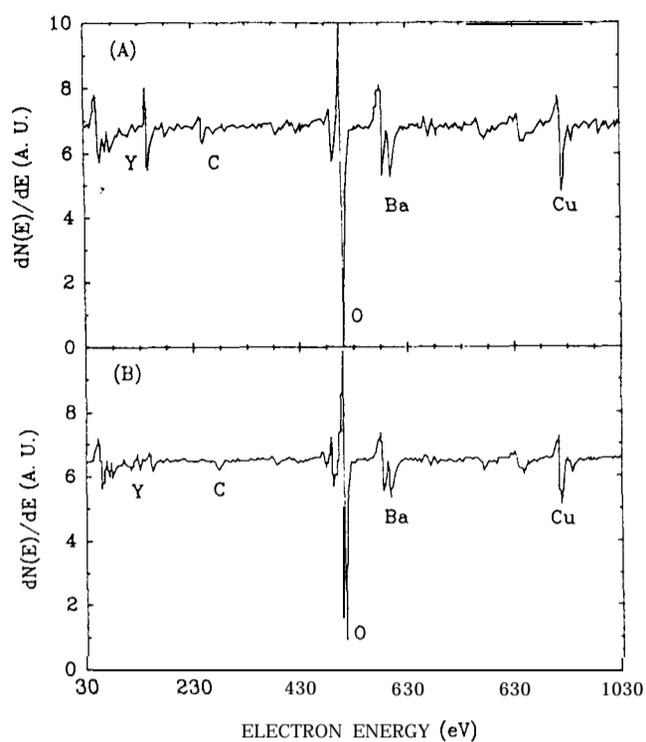


FIG. 4. (A) AES spectra of $\text{YBaCuO}/\text{Al}_2\text{O}_3/\text{Si}(100)$. (B) AES spectra of $\text{YBaCuO}/\text{LiNbO}_3$.

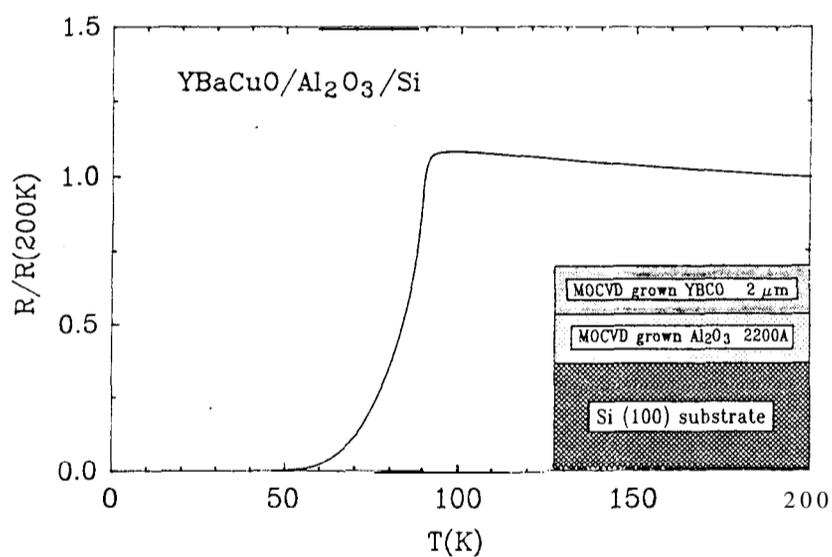


FIG. 5. R-T curves of $\text{YBaCuO}/\text{Al}_2\text{O}_3/\text{Si}(100)$. The insert shows the layer diagram

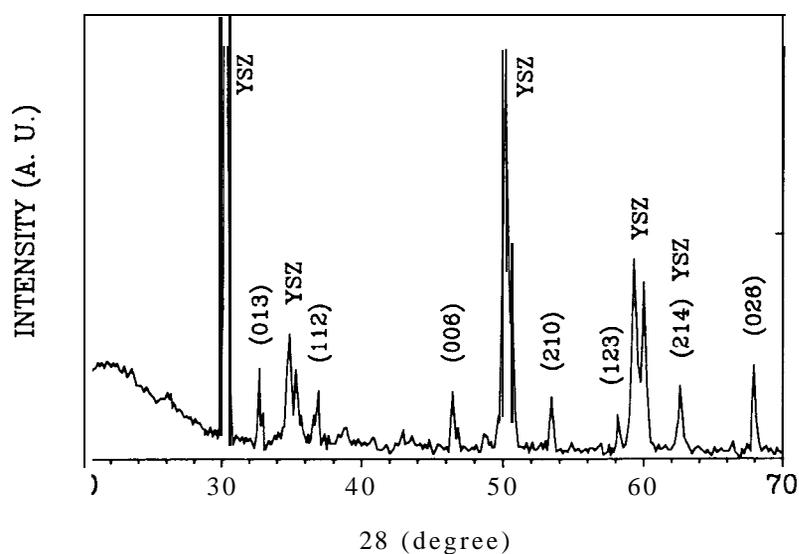


FIG. 6. XRD of YBaCuO/p-YSZ.

1-2-3 phase without residual carbon participation. The film interface between YBaCuO and $\text{Al}_2\text{O}_3/\text{Si}$ was not clear from the AES depth profile because of chemical reaction. Aluminum was detected in the YBaCuO layer near the interface, but no Si was observed. The interfacial reaction severely contributes to diffusion of a large amount of aluminum into the film. Barium significantly penetrated into the Al_2O_3 layer. We believe that formation of the Ba-rich layer at the interface was caused by migration of barium toward the interface. Although there is a chemical reaction at the YBaCuO/ Al_2O_3 interface, Al_2O_3 is limiting diffusion of Si in the YBaCuO layer at the high deposition temperature of 800 °C. The deposition relationship between YBaCuO and the substrate is likely to be complex and to change with deposition conditions such as substrate temperature and deposition rate. Further work is under way to improve the quality of the samples. We believe that use of N_2O gas as an oxidizer at a low system pressure of 10 Torr is useful to *in-situ* MOCVD growth.

In summary, we have successfully deposited the YBaCuO thin films on single crystalline LiNbO_3 and Al_2O_3 buffered Si substrates by *in-situ* MOCVD. A thin buffer layer of Al_2O_3 appeared to be a γ -phase hetero-epitaxial growth by MOCVD. Although interface reaction of Al and Ba happened, the buffer layer is good at limiting diffusion of Si into the YBaCuO layer. N_2O gas is an efficient oxidizer for preparing the films without post annealing. An *in-situ* growth technique is useful for future hybrid superconductor-semiconductor and integrated optical device applications.

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