Crystal engineering of high- T_c and related oxide films for future electronics

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Abstract. Advanced technology and future prospect of oxide-based electronic materials are described with a focus on the significance of atomically controlled epitaxy of high- T_c superconductors and related oxide films. Problems in suitably forming the oxides whose power is potentially superior to silicon's are discussed to stimulate technology development for engineering oxide film growth on an atomic scale. Our experimental results on controlled epitaxial growth of oxide films are presented with respect to pulsed laser deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films as well as laser MBE growth of SrTiO_3 homoepitaxy and CeO_2 heteroepitaxy on Si substrates.

Keywords. Crystal engineering; high- T_c superconductor; oxide electronics; laser MBE; atomic layer epitaxy.

1. Introduction: New era of oxide research

Electronics is the driving force of civilization and innovation today and this situation is likely to continue in the 21st century. The most important material in current electronics is silicon, and this status of silicon is also likely to remain for centuries. Nevertheless, we are tempted from time to time to pose the question whether we will find or develop an electronics material superior to silicon.

Electronics application of oxide materials includes use as insulators, capacitors, piezo- and pyroelectric devices, solid ionics, varistors and transparent conductors, as well as magnets and optical devices. These oxides are used in both bulk form and as thin films mostly in polycrystalline phase. The so-called fine ceramics technology is based on the control of grain size in micrometre scale. With progress in microelectronics, much attention has been focussed on the fabrication of thin films, especially in high-quality single-crystal (epitaxial) phase. A current concern in the development of larger integrated silicon electronics is focussed on high-dielectric oxide films for capacitors and nonvolatile memories. In this respect, especially interesting is the heteroepitaxial growth of perovskite-type oxide films on silicon substrates. Extensive studies are being conducted for this purpose by using various methods such as vacuum evaporation, sputtering, chemical vapour deposition (CVD), sol-gel process, pulsed laser deposition, and molecular beam epitaxy (MBE). Films so far fabricated are, however, not so extraordinary, since they have crystal structures of known perovskite type or a slight modification and their properties are within our imagination.

In today's most advanced electronics research, much attention is paid to the fabrication of artificially designed structures to verify new device concepts based on quantum effects. As these are primarily important technology, intensive studies are performed on atomic-scale control and characterization of semiconductor thin films and heterostructures. In contrast, until recently we had neither a strong need for atomically engineered oxide films nor a theoretical background for predicting characteristic properties or practical application of such films. Under these circumstances,

few people were interested in developing the technology of fabricating atomically regulated oxide films.

The discovery of high- T_c oxide superconductors (Bednorz and Muller 1986) changed the situation. The high- T_c superconductivity in layered cuprates was beyond our imagination and this surprising quantum effect suggested further potential of complex oxides in which electrons and spins are strongly correlated. As a systematic experimental approach to the exploration of potential and mystery of oxides, people started realizing the significance of atom technology of oxides (Koinuma and Yoshimoto 1994). This article is intended to stimulate and discuss the possibility of oxides as new innovative electronic materials with focus on the following features:

- (i) Intrinsic properties of oxides compared with silicon
- (ii) Crystal engineering of oxides for the fabrication of artificially designed crystal lattices and heterostructures including high- T_c superconducting tunnel junction (Koinuma 1994)
- (iii) Combination with silicon electronics
- (iv) Exploration of novel functionalities in oxides.

2. Silicon versus oxides

Compound semiconductors were once considered good candidates to displace the position of silicon because of their compositional and functional versatilities. However, they are still far from replacing silicon in the electronics market. One of the main reasons is the lack of high-quality insulators that can be combined with them in device fabrication. From a materials science viewpoint, the great success of silicon electronics rests on relatively simple features: (i) the availability of large-size and defect-free single crystals, (ii) valence control by impurity doping, and (iii) the presence of high-quality SiO_2 insulators. The third advantage of SiO_2 , may no longer exist in further integrated silicon devices due to the low dielectric constant of SiO_2 and the existence of defects at the interface between crystalline silicon and amorphous SiO_2 .

Oxides have a far broader spectrum of structures and properties than does silicon. Oxides with similar crystal lattices may have insulating, semiconducting, metallic and

Table 1. Characteristics of silicon and oxides.

	Si/ SiO_2	Oxides
Components	SiO	Various metals, O
Intrinsic properties	Semiconductor (Si) Insulator (SiO_2)	Insulator; semiconductor; metal; superconductor; ferro-; piezo-; pyro-electricity; ferromagnetism; optical functions; nonlinearity in electric, magnetic and optical properties, ...
Doping	Substitutional	Cation substitution Oxygen nonstoichiometry (chemical)
Crystal structure	Diamond (Si) Amorphous (SiO_2)	Versatile: rock salt, fluorite, zinc blende, spinel, perovskite, etc.

Figure 1. Unified layered lattice structure of perovskite-based functional oxides.

superconducting properties, as well as other functional properties, as summarized in table 1. Based on sophisticated crystal engineering techniques for oxides, it would be possible to fabricate all epitaxial hybrid devices and multiply stacked modules. Among a variety of oxides, special emphasis should be placed on perovskite oxides because this group of compounds represent functional ceramics and have good lattice matching among themselves as well as with silicon. Figure 1 represents the lattice structures of typical perovskite and high- T_c superconductors. Although many new high- T_c cuprate superconductors have been claimed to be discovered, their crystal lattices can be unified into a modified perovskite structure in which there is slight change in one or two atomic layers in the repeating unit. Hence, layered lattices related to high- T_c cuprates could be reconstructed and/or modified if we establish the technology of assembling two-dimensional lattices of one to several atomic layers with designed compositions.

3. Crystal engineering of oxides: Why and how?

Ever since our first success in superconducting La–Sr–Cu–O film deposition in early 1987 (Koinuma *et al* 1987), extensive studies have been conducted on the fabrication of high- T_c oxide films and devices. Success has been achieved to some extent in relatively simple devices using plain superconducting films or grain-boundary (Dimos *et al* 1988) and step-edge junctions (Daly *et al* 1991). Nobody, however, has succeeded in fabricating an SIS (superconductor–insulator–superconductor) tunnel junction that shows a clear hysteresis in I – V characteristics at a temperature above 77 K. Such a junction is presumably the key to the wide electronic device application of high- T_c superconductors, for example for switching devices expected to work much faster than conventional semiconductor transistors.

3.1 Elementary processes for SIS tunnel junction

The difficulty in fabricating SIS tunnel junction originates, evidently, from the very short (3–20 Å) coherence lengths of high- T_c superconductors. This necessitates not only high-quality but also atomic-scale engineering of both superconducting and insulating films. Such thin-film technology is almost established in semiconductors,

Table 2. Criteria of SIS device quality superconductor and insulator.*Superconductor*1. *Bulk*

Good electronic properties

2. *Surface*

No deterioration in superconductivity

Homogeneity in superconductivity

Atomically flat

Particle free *Well equilibrated and
relaxed lattice matrix**Insulator*

Good insulator

Surface flatness in atomic scale

Perfect interface with YBCO

Thickness control in atomic scale

Figure 2. (Left) STM image of YBCO (001) surface taken at a constant current of 15 pA and a tip bias voltage of 500 mV. (Right) Tunnelling spectra taken at a set point current of 4 nA and a tip bias voltage of -100 mV.

but similar methods cannot be simply applied to high- T_c oxides due to some specific features originating from the ionic bond character, the multicomponent nature of the material, and mobile oxygen in the crystals. Other problems include the lack of high-quality single-crystal substrates and immaturity of supporting technologies such as substrate cleaning.

Problems to be solved for the fabrication of SIS tunnel junction (if possible) are listed in table 2. Most of these hurdles are presumed to have been overcome judging from the results we have accumulated. Some such results are exemplified in figures 2, 3, 5–7. Chemical stability and superconductivity even at the topmost surface were verified by the simultaneous observation of atomic image and superconducting

energy gap in the cryogenic STM/STS measurements on an air-exposed c -axis-oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) film (figure 2) (Nantoh *et al* 1994). This highly crystalline and stable film was fabricated by pulsed KrF-excimer laser deposition under conditions optimized to give a well-relaxed (quasi-equilibrated) structure and a high oxygen content ($0 < \delta < 0.1$). Although the c -axis-oriented YBCO films exhibit good superconductivity ($T_c > 90$ K, $J_c > 10^6$ A/cm² at 77 K), they have a very short coherence length (~ 3 Å) and are apt to have a lot of precipitates on the surface especially in high-quality films (Gong *et al* 1994). a -Axis-oriented films have much less precipitates on the surface and a longer coherence length than c -oriented films, but instead they tend to have cracks and poor superconductivity. By controlling the deposition conditions and using an appropriate substrate, we could prepare high-quality a -oriented films with smooth surfaces and T_c exceeding 85 K (figure 3) (Koinuma *et al* 1994).

Figure 3. SEM (a) and RHEED (b) patterns of a -oriented YBCO film prepared by temperature gradient PLD (pulsed laser deposition) method.

Figure 4. Laser MBE system equipped with *in situ* RHEED and XPS.

Figure 5. AFM image of BHF (NH₄F–HF)-treated SrTiO₃ substrates. The vertical profile was taken along the line indicated in the image. The BHF-treated substrate exhibited atomically flat terraces and 0.4-nm-high steps.

Figure 6. The RHEED intensity variation during homoepitaxial growth of SrTiO_3 by laser MBE (a) on the commercial SrTiO_3 and (b) on the BHF-treated SrTiO_3 .

Figure 7. The variation of RHEED intensity during the heteroepitaxial growth of STO on a -axis-oriented YBCO. (a) Specular spot and (b) central streak.

In view of such a short coherence length even in *a*-oriented film, I (insulator) layer thickness must be regulated on an atomic scale. Elementary processes to fulfil this requirement are summarized in table 3, and can be achieved by the laser MBE (pulsed laser deposition in ultrahigh vacuum condition), which we employed for the first time for oxide film deposition (Yoshimoto *et al* 1990). The thermodynamical problem of oxidizing metal components in high vacuum can be overcome by the use of such a highly oxidizing agent as ozone or NO₂. Homo- and some heteroepitaxial growth of oxides were performed by the laser MBE system illustrated in figure 4. In the system, a reflection high-energy electron diffraction (RHEED) apparatus, an X-ray photoelectron spectrometer (XPS), and a metal evaporator are installed for *in situ* measurements of growth process, composition and valence analyses of film, and electrode deposition without exposing the film in air, respectively.

RHEED intensity oscillation, which verifies atomically regulated layer-by-layer epitaxial growth, was confirmed for laser MBE growth of SrTiO₃ and so-called infinite layers of ACuO₂ (A = Ca, Sr, Ba, or mixtures) on SrTiO₃ substrates as well as for CeO₂ growth on Si(111) substrate. The oscillations, however, were not so sharp and damped gradually when the films were grown on the substrates supplied commercially and treated with the conventional cleaning procedures. Then we developed new surface treatment procedures to make single-crystal SrTiO₃ and sapphire surfaces composed of atomically smooth terraces and steps of one or two atomic layers in height. Figure 5 shows the atomic force microscopy (AFM) image of SrTiO₃ surface defined atomically by a wet cleaning treatment. The use of this substrate enabled us to observe the RHEED intensity oscillation as perfect as those in matured MBE growth of semiconductors during homoepitaxial laser MBE growth of SrTiO₃ (see figure 6) (Kawasaki *et al* 1994). The oscillation periodicity corresponds well with one unit cell growth (3.9 Å). Oscillation was also observed as shown in figure 7, although not so perfect as in figure 6, during the laser MBE growth of SrTiO₃ on *a*-oriented YBCO film. Thus, we can regulate SrTiO₃ layer thickness digitally by counting the oscillation peaks and use this technology for the formation of SIS junction.

3.2 Approach to new materials and phenomena

High-*T_c* oxides have a tendency of increasing *T_c* with increase in the number of CuO₂ plane in a layered perovskite unit cell structure, represented in figure 1. Thus the atomically controlled epitaxy of oxides is also promising for the exploration of new

Table 3. Elementary processes and characterization of ceramic layer epitaxy.

Process	Characterization
Oxidation in UHV	Thermodynamics and kinetics XPS
Epitaxial growth	RHEED pattern XRD
Lateral growth	RHEED oscillation
Atomic and valence control in as-grown film and interface	XPS (<i>in situ</i>)

Table 4. CeO_2 film orientation prepared by laser MBE on Si substrate at 600°C .

Film	Substrate	Orientation	
CeO_2	Si-O/Si	$\text{CeO}_2(111)$	In-plane random
	Si(001)	$\text{CeO}_2(110) \parallel \text{Si}(001)$	$\text{CeO}_2[110] \parallel \text{Si}[110]$ and $\text{CeO}_2[001] \parallel \text{Si}[110]$
	Si(110)	$\text{CeO}_2(111) \parallel \text{Si}(110)$	$\text{CeO}_2[001] \parallel \text{Si}[110]$
	Si(111)	$\text{CeO}_2(111) \parallel \text{Si}(111)$	$\text{CeO}_2[110] \parallel \text{Si}[110]$

Figure 8. Temperature dependences of resistivity for $(\text{SrVO}_{3-x}; 2 \text{ units}/\text{SrTiO}_{3-y}; 1 \text{ unit})_n$ superlattice measured using currents varied from 0.001 mA to 10 mA .

superconducting materials. Infinite-layer cuprates, ACuO_2 ($A = \text{alkaline earth metal}$), were prepared by atomic and unit-cell-layer epitaxies using conventional and laser MBE to examine their superconductivity (Kawai *et al* 1993).

Key factors and process parameters for constructing artificially designed crystal lattices should include lattice matching between the bottom and growth layers, Coulomb interaction at the heterointerface to be formed, oxygen control under the film deposition conditions, and setting conditions for surface migration to achieve two-dimensional growth. This crystal engineering technology is more advanced than the conventional sequential deposition by multitarget sputtering or pulsed laser deposition. *In situ* diagnosis of the surface reactions and interface characterization are indispensable for quantitative control and evaluation of the film growth. Once we have this new materials technology, we can even use it to search for new properties and physical phenomena. Besides high- T_c superconductivity, a few interesting phenomena have been observed and predicted in recent years on bulk complex oxides as well as on thin films and layered hetero-structures. Figure 8 shows the anomalous conducting behaviour we detected in the digitally controlled superlattice of $\text{SrTiO}_3/\text{SrVO}_3$. This apparent metal-semiconductor transition at about 100 K can be regarded as one of the new phenomena in low-dimensional conductive oxides (Koinuma *et al* 1991).

4. Combination of oxides with silicon

An atomically controlled formation of hetero-junctions between oxides and semi-conductors is desired for the development of highly integrated devices. The growth of high-dielectric or ferroelectric perovskite oxides on silicon is extensively studied for use in capacitors and gate insulators. SOI (silicon on insulator) also attracts much interest to stack layers of silicon devices.

CeO₂ has a fluorite structure with excellent lattice matching with Si (99.6% at room temperature). CeO₂ can be used as a buffer layer for the epitaxial growth of high-*T_c* superconducting films on Si. The lattice mismatches between cuprate superconductors and Si are less than 1% in their *a*–*b* planes. For the deposition of oxide films on Si, we encounter such a contradicting process condition as oxygen control without oxidizing the Si surface. CeO₂ was considered suitable for film deposition on Si because the oxygen affinity of Ce is high enough to form CeO₂ in ultrahigh vacuum. Thermodynamically, *x* in CeO_{*x*} is higher than 1.99 at 1000°C under 7.6×10^{-9} torr of oxygen.

Films were grown on clean Si substrates heated at 600–800°C by ablating a CeO₂ target under 10^{-9} torr pressure. Table 4 summarizes the growth behaviour of CeO₂ films on Si single crystals. The epitaxial CeO₂ films were obtained on Si(111) but not on Si(001) or Si(110). These results are well explained in terms of preferential arrangement

Figure 9. Cross-sectional lattice image at the interface observed from $\langle 110 \rangle$ direction for the CeO₂ film grown on Si(111) at 20°C. The arrow indicates the interface. CeO₂ film grew epitaxially with the same crystallographic orientation as that of Si(111). No boundary amorphous layer was formed at the interface.

of the first plane of growing CeO_2 by its Coulomb interaction with the topmost Si surface. Some other oxides such as SrTiO_3 and yttria-stabilized zirconia (YSZ) were grown epitaxially on Si substrate. Epitaxial growth of CeO_2 on Si(111) at room temperature was recently achieved by laser MBE to give such a sharp interface as depicted in figure 9. The interface is hardly distinguishable by transmission electron microscopy. This epitaxial CeO_2 film has a dielectric constant much higher than that of SiO_2 and a very high breakdown voltage.

5. Conclusion

Sophisticated pulsed laser technology has been used successfully to fabricate atomically controlled films of high- T_c superconductors and related complex oxides as verified by the observation of RHEED intensity oscillation persisting for more than 300 cycles during homoepitaxial SrTiO_3 growth. Such technology could be extended to the deposition of oxide films on silicon with almost perfect heteroepitaxial interface. Such crystal engineering of oxides is expected to lead to the fabrication of high- T_c Josephson tunnel junction, and to be useful in advanced silicon VLSI technology and furthermore in novel electronics based on all epitaxial oxide films.

Acknowledgements

The research described in this article was done in collaboration with my colleagues Drs M Yoshimoto and M Kawasaki as well as with graduate students T Maeda, N Kanda, K Fujito, K Takahashi, R Tsuchiya and T Ohnishi, to whom I would like to express my sincere thanks. The research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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