Construction and Superfunction of Metal-oxide Nanostructures and Interfaces(Interfaces by various techniques)

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Construction and Superfunction of Metal-oxide Nanostructures and Interfaces

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Metal oxides show such versatile properties as high T_C superconductivity, ferroelectricity, colossal magnetoresistance and non-linear optical properties. By developing laser molecular beam epitaxy, we have been working on atomic scale control for the heteroepitaxy of these materials in order to explore a novel field of "oxide electronics", in which monolithically integrated devices composed of epitaxially grown oxide nanostructures show outstanding performances that Si-based semiconducting devices would not be able to give. Among many topics we have, we concentrate on Josephson tunnel junction made out of high T_C superconductors and ultra-violet laser emission from ZnO nanocrystal films.

KEYWORDS: metal-oxide, nanosturuture, epitaxy, laser MBE, Josephson junction

1. Oxide epitaxy directed towards oxide electronics

Epitaxial technology of metal-oxide materials has been drastically improved in the decade because the discovery[1)] of high critical temperature superconductors (HTSC) triggered intensive studies of film preparation not only for device application but also for basic physics studies. Now, such low density integration devices as microwave components and magnetic sensors can be readily fabricated using HTSC epitaxial films, but we still need further progress for making atomic scale control of the hetero-interface. One of the most important device elements in superconducting electronics is the Josephson tunnel junction, of which two superconducting electrodes (S) are separated by a very thin insulating barrier film (I). I layer must be uniform and pinhole-free to prevent short but the film thickness must be comparable with the coherence length, i.e. the size of Cooper pairs, (0.5~1.5 nm depending on the direction in the anisotropic crystals) to allow them tunnel across I layer. This severe condition require atomic scale control of oxide epitaxy. This is why none of successful tunnel junction has been reported regardless enormous efforts paid for the last 10 years.

Atomic technology of oxide is not just for tunnel junctions but should explore a novel field of ceramics research[2)]. Figure. 1 represents a unified crystal structure of HTSC's and their basic constituent, i.e., perovskite structure. If we take two dimensional growth of the film into account, the perovskite (ABO_3) can be considered as an alternating stack of AO and BO_2 atomic layers. Almost all of HTSC

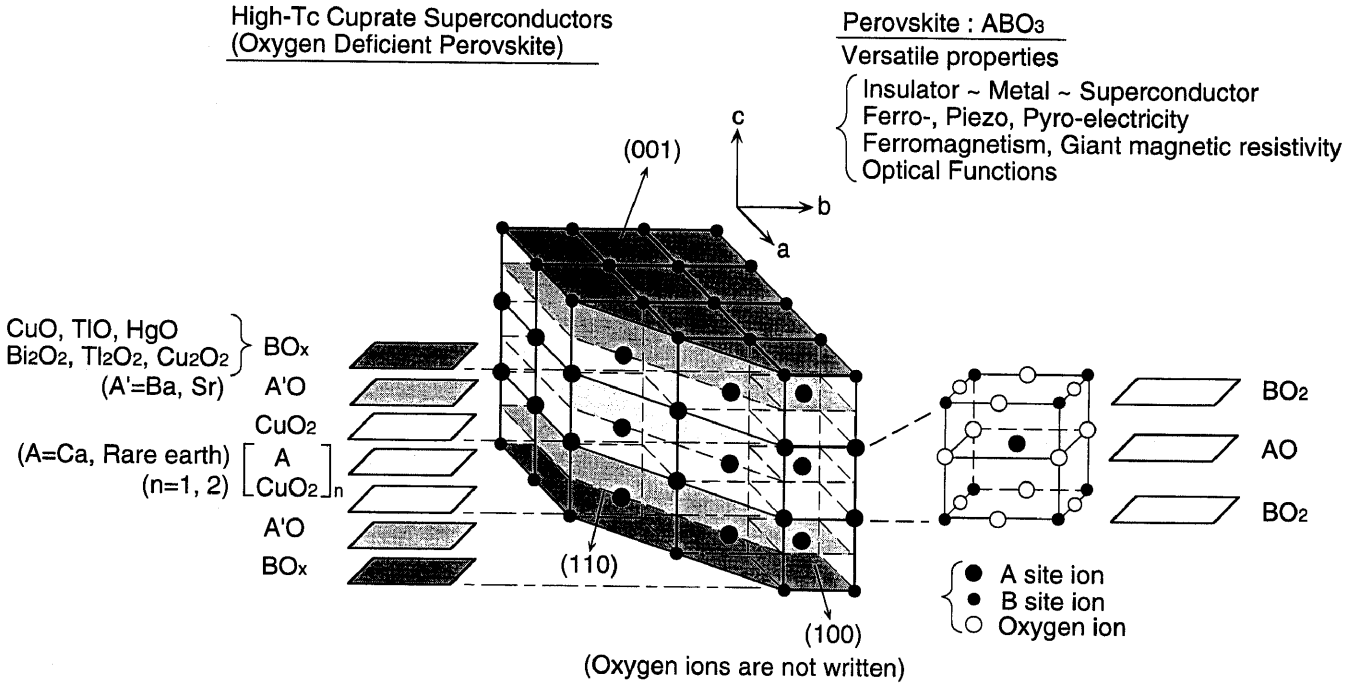

Figure 1. Layer lattice image (atomic layer model) commonly applicable to high-Tc (>77K) superconducting oxides, as compared with typical perovskite oxide.

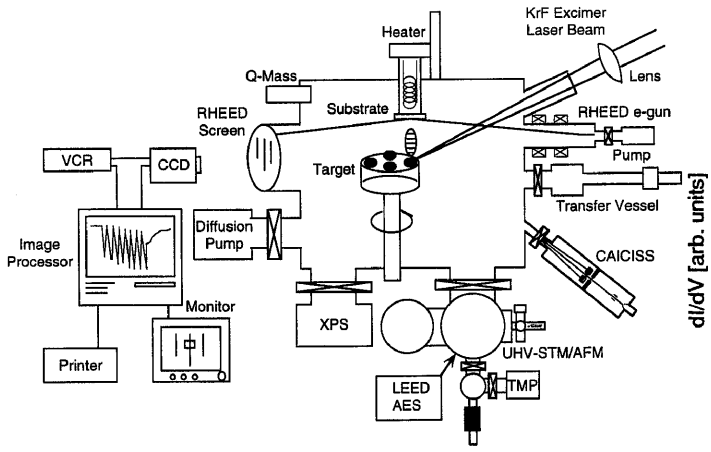

Figure 2. Schematic diagram of laser MBE system.

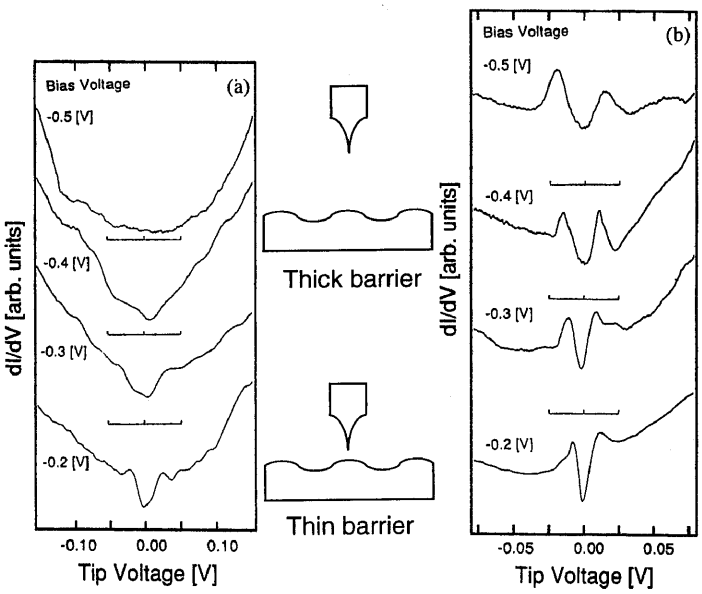

Figure 3. Bias voltage dependence of the tunneling spectrum of the (a) (001) and (b) (110) surface of a YBCO thin film at 4.2K. Tip-bias voltage are -500mV, -400mV, -300mV, and -200mV, respectively. The set point current is constant, 2nA. The zero conductance value is shown by the line under each spectrum.

materials can be constructed by properly accumulating various AO and BO_2 layers. If we get a capability of artificially accumulating these atomic layers as we design, we should be able to construct new layered compounds which might have superfunction. Actually, by looking around the existing perovskite compounds, one can find out such versatile properties as listed in Fig. 1. Number of d-electrons in transition metal at B-site, i.e., the kind of element and its valency, is a dominant factor for the selection of properties. The size and valency of A site ion determine crystal size and carrier concentration, respectively. Therefor, these flexibility provides with the opportunity of fine tuning of the properties. If one could monolithically integrate various devices composed of fully epitaxial oxide heterostructures, one should be able to explore a new field of electronics with versatile superfunction that standard semiconductor devices would not be able to show.

In this paper, we show our aim and recent progress by briefly reporting on atomic scale characterization and control of oxide nanostructure.

2. Laser MBE

For just making epitaxial oxide films, pulsed laser deposition (PLD) is especially suitable for quick lab-research. However, in order to realize atomic scale control needed for the feasibility study of oxide electronics, one has to combine PLD with atomic scale analytic techniques. One of our originally designed and constructed equipment is shown in Fig. 2[3]. Ceramic target is ablated by excimer laser pulses to deposit films. In-site reflection high energy electron diffraction (RHEED) observation enabled us not only to examine surface structure but also to monitor and control layer-by-layer growth by its intensity oscillation. Crucial factor to apply RHEED for oxide materials was the quasi-thermodynamic consideration of effective oxygen activity for various oxygen containing gas species[4].

3. Low temperature scanning tunneling spectroscopy

As shown in Fig. 1, the crystal structure and electronic properties of HTSC are highly anisotropic. For designing the tunnel junction, we examined the anisotropy of coherence length by means of scanning tunneling microscopy (STM) operating at 4K. The specimens were (001) and (110) oriented YBCO thin films having very high crystallinity. On both surfaces, clear atomic images were obtained even for the films exposed to air before STM measurement, indicating that YBCO film surface can be very stable. On such well defined surfaces, density of states were recorded at various surface-tip distances. On (001) surface, superconducting gap structure (Δ~20meV) could be seen only when the tip is close to the surface. Whereas, the gap structure always appeared in the spectra taken on (110) surfaces as far as the tunneling current was detected. These results indicate that the decay of superconducting wave function into vacuum along c-axis is much shorter than that in the a-b plane[5]. When S-I-S structure is to be prepared in a sandwich fashion, one should use (100) or (110) oriented YBCO films as electrodes for taking the advantage of larger coherence length.

4. Atomically defined substrate surface and epitaxy

If one wish to control the film growth in an atomic scale, substrate surface has to be regulated in the same scale. Commercial $SrTiO_3$ (100) substrates most popularly used for HTSC films are fairly flat and comparable to Si wafer surface without any special treatment. However, this surface is not smooth enough for atomically regulated epitaxy of HTSC and related compounds. Atomic force microscopy picture in Fig. 4 represents the $SrTiO_3$ surface treated in a buffered HF-NH_4 solution (BHF: pH=4.5) for 10 min. The surface is composed of 0.4nm (unit cell) high steps and

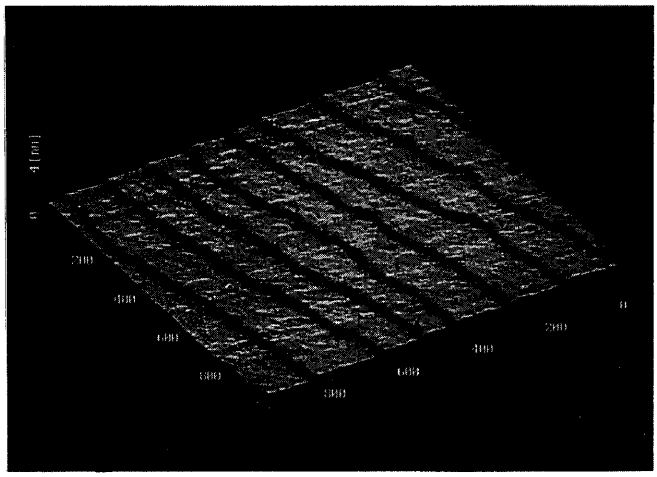

Figure 4. AFM image of the $SrTiO_3$(001) substrate treated with NH_4F-HF (pH-4.5) solution. The step height is 0.4 nm and terrace width is 150 nm.

atomically flat terraces. We found the BHF solution selectively etched the SrO atomic layers of $SrTiO_3$ for giving an atomically flat surface of which topmost surface was terminated by TiO_2 atomic plane[6].

This surface treatment was a kind of breakthrough for us to achieve really atomic scale control of oxide epitaxy. One of the examples is demonstrated in Fig.5, where RHEED intensity oscillation persists hundreds of cycles for the laser MBE growth of homoepitaxial $SrTO_3$ films. When the film growth was stopped at one of the minimum in RHEED

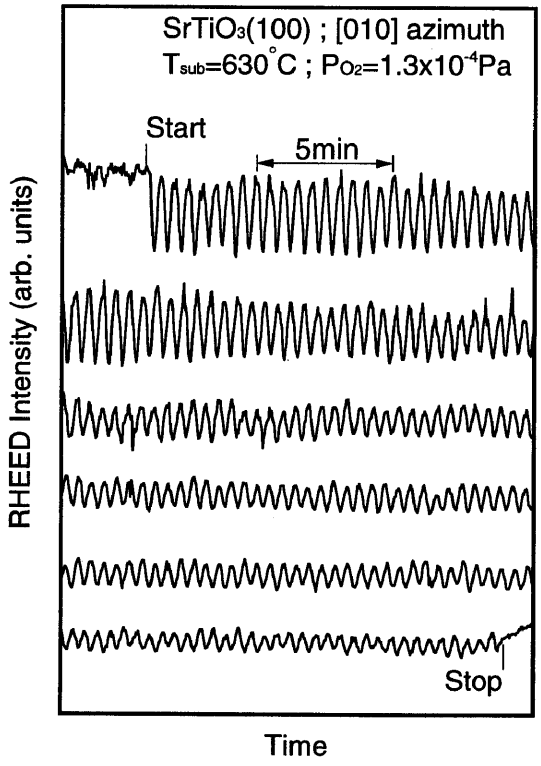

Figure 5. RHEED intensity oscillation observed on the specular spot during homoepitaxial growth of $SrTiO_3$ on BHF treated substrate.

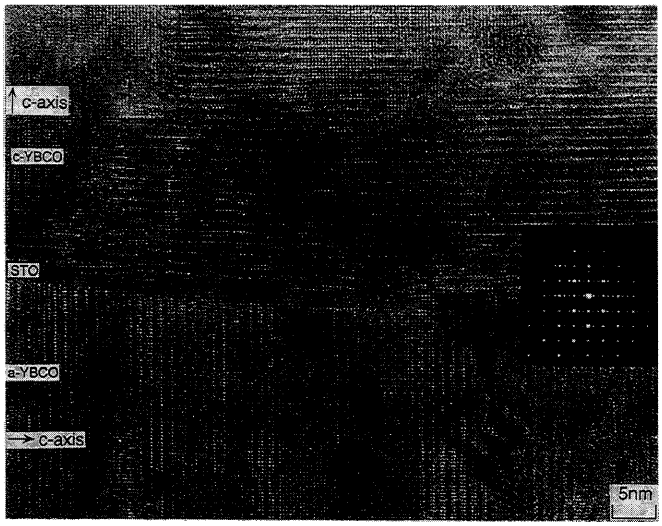

Figure 6. The cross-sectional TEM image of S-I-S heterostructure for the device composed of (001) YBCO / $SrTiO_3$/ (100)YBCO.

intensity, we found a lot of islands with height of 0.4nm nucleated on the original terraces[6]. When the growth was terminated at the peak of the oscillation, the surface was similar to that shown in Fig. 4. Commercial as-polished substrate had never allowed us to perform such a perfect layer-by-layer growth.

5. S-I-S trilayer junction

We have been preparing S-I-S heterostructures with using (100) YBCO films as the bottom electrode. We encountered and have solved such severe problems as orientation control[7], cracking[8], and precipitate formation[9]. The details are out of the scope of this paper[5, 10, 11]. We just show one of TEM pictures which shows (001) YBCO / $SrTiO_3$ / (100) YBCO. The orientation of YBCO electrodes were successfully controlled and the thickness of $SrTiO_3$ was found out to be 4.8nm as we had designed. We are patterning the device structure and characterizing the device performance.

6. A novel optical property of nanocrystal ZnO

Besides perovskite type oxides, we have been interested in wurtzite type ZnO as a material for light emission. ZnO has a bandgap of 3.5eV and ultraviolet emission can be expected for the bandgap recombination. For short wavelength light emitting diodes and lasers, GaN and its related solid solutions have attracting considerable attention. Here we propose ZnO as an alternative candidate for these devices.

ZnO thin films deposited by laser MBE were epitaxial but composed of self-assembled hexagonal nanocrystals whose size (50-250nm) can be tuned by deposition conditions. The photoluminescence of the films showed sharp free-exciton peak at 3.3eV and hardly show midgap emission around 2.2eV, which has been reported to be dominant for poor quality films. When the film is excited by frequency tripled Nd:YAG laser beam (355nm, 15ps) at

room temperature, intense emission was observed at 3.2eV (388nm). We concluded that the emission is due to the excitonic stimulated emission. For facilitating the excitonic emission and cavity formation, the natural grain boundaries between nanocrystals play essential role. Details will be reported elsewhere[12].

7. Conclusion

We have shown why we are interested in and how we have been achieving atomic controls of oxide epitaxy. As superfunctions of oxide nanostructures, we have picked up Josephson effect in HTSC tunnel junction and ZnO lasing to show the possibility and potential of oxide electronics.

Acknowledgements

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