In-situ Work Function Measurement of Molecular Beam Epitaxy Film Surface Using RHEED-Beam Excited Secondary Electron Peaks

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The relative work function of growing surface of molecular epitaxy films was measured *in situ* using the energy shifts observed in secondary electrons excited by reflection high energy electron diffraction beam.   In the case of a superconducting perovskite $YBa_2Cu_3O_x$ the measured work function showed different behaviors between the coevaporation and the sequential evaporation of the metal elements reflecting differences in the electronic structures of the growing surfaces.

1. Introduction

It is well known that since the onset of the secondary electron energy from a solid surface depends on the work function of the solid, the relative work function for a sample surface can be determined from an energy difference of the onset between the sample and a standard substance with the known work function.   We previously reported the results of *in-situ* composition analysis of a growing film surface using a homemade reflection high-energy electron diffraction (RHEED) beam excited Auger electron spectroscopy (AES) system [1].   The system employs a compact energy analyzer in a differentially pumped box and enables real time measurement of the energy of electrons emitted from sample surface even in conditions such as film deposition in an oxidizing atmosphere. The availability of the system was demonstrated by the real time monitoring of the elements in the top layer of a material with layered structures, typically, perovskite oxide superconductors, during its growth [1].   Although the top layer in the most stable structure of these materials could be estimated theoretically, it must have been clarified by *in situ* observation during the film growth.

However, in the case of the oxide superconductor, because there should be strong electronic interactions between layers to show such high T_c, it was desired that the electronic states of the top layer could also be measured *in situ* by the method other than AES.   For this purpose in the present study the work function of a growing crystalline film surface during molecular beam epitaxy (MBE) has been determined using the same system.

2. Experimental

The energy diagram for a system consisting of two samples and a spectrometer is schematically shown in Fig.1.   As easily understood from the diagram, the work function difference of the samples, $\Delta\Phi$, can be measured as the onset energy shift of the secondary electrons, ΔE.   Therefore if the work function of either sample was known, the work function of the other would be determined simply as,
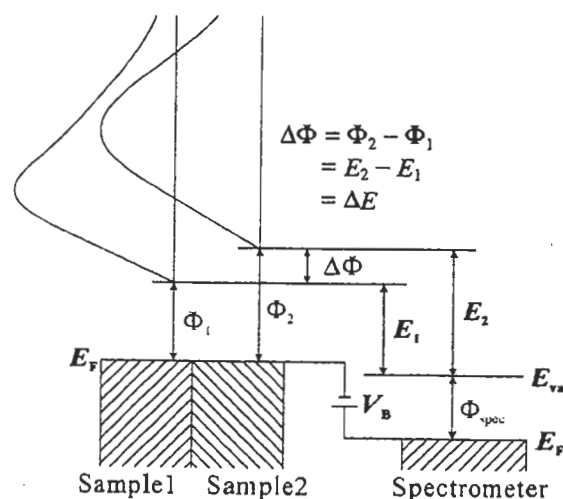
$$\Phi_2 = \Phi_1 + \Delta E. \qquad (1)$$

Figure 1. Schematic diagram showing the measurement principle for determining relative work function by onset energy of secondary electrons.
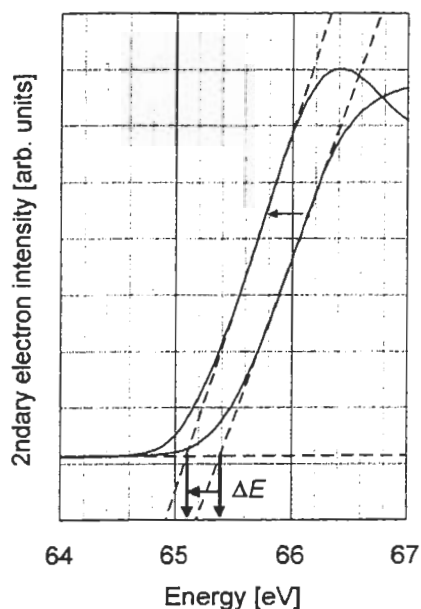
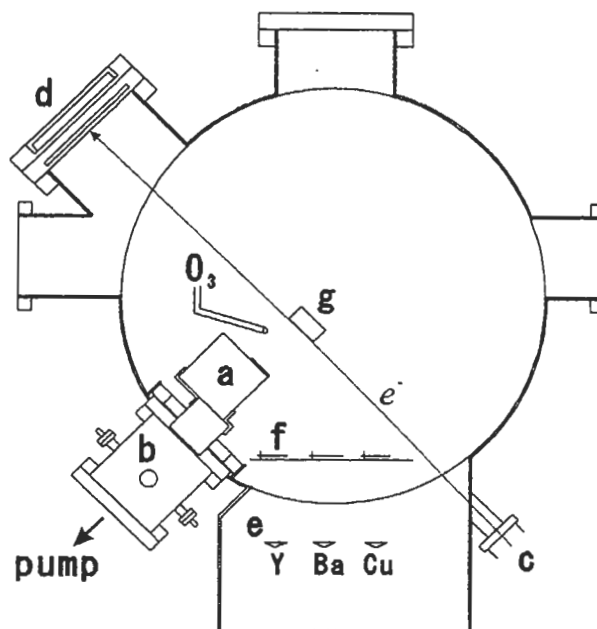Figure 2. Straight line fitting to find onset of secondary electron peaks.

Figure 3. Cross sectional view of RHEED-SES system; a. Energy analyzer system. b. Manifold for electric wiring. c. RHEED electron gun. d. RHEED screen. e. Metal sources.   f. Shutters. g. Substrate.

Figure 2 shows how the onset of the secondary electron peaks were actually determined.   The uncertainty of the energy position determined by this method is considered to be less than 0.02 eV as shown later.

The cross section of the RHEED-beam excited secondary electron spectroscopy (SES) system is shown in fig.3.   The system is essentially identical to the RHEED-AES system for which the details have already been reported [1].   Briefly the system consists of a compact sector-type energy analyzer (r_{outer} = 27.8 mm) in a shielding box and a conventional RHEED system equipped to an MBE chamber with more than three metal sources either in electron beam heated crucibles or effusion cells. The analyzer box is differentially evacuated with a magnetic-bearing turbo molecular pump so that the analyzer can work even if the chamber is filled with a reactive gas such as ozone.   The distance between the substrate and the aperture of the analyzer box is 35 mm.   Since the secondary electron yield is larger by more than 100 times than Auger electron yield, the energy resolution has been improved from 0.8 eV at AES to 10 meV and small differences of the work function during film deposition could be measured.

In order to prepare oxide films in MBE conditions, highly concentrated (more than 90 vol.% at the outlet of the line) ozone gas is introduced from a homemade ozone jet generator [2] to the chamber up to 5×10^{-4} Pa.   YBa$_2$Cu$_3$O$_x$ (YBCO) films were deposited by two different modes to investigate the film growth mechanism.

One is coevaporation mode in which all the metals were supplied to the substrate at the same time while the other is sequential evaporation mode in which the metals were supplied to the substrate one by one using the shutters in the order so as to form, if possible, the perovskite structure of YBCO units (see Fig. 4) *layer by layer*.

Figure 4. Unit structure of YBa$_2$Cu$_3$O$_x$

3. Results and Discussion
Work function of SrTiO$_3$ substrate

The relative work function of SrTiO$_3$ (STO) to that of gold was determined by RHEED-SES of the STO substrate during the deposition of gold evaporated by an electron beam.   The STO was preannealed at ca. 400 C in ozone to get clear flat (100) surface [1].   Figure 5 shows the evolution of the onset of the secondary electron peaks during the deposition of gold at ca. 400 C for two sets of data. The values are shifted so that the final data points match the work function of gold (5.1 eV [3]).   The difference in work function change during Au deposition at small thickness is probably due to the surface morphology difference in the two data sets.

Au was not epitaxially deposited on STO and thus its morphology. at small thickness was not controllable resulting in either a flat film or island-like patches.   When Au layer reaches a certain thickness, then the work function change stays constant. Thus the work function of STO, Φ_{STO}, may lie in 4.84-4.88 eV if the correction for the high temperature is negligible.   As STO is a semiconductor at the experimental conditions [4], the energy diagram shown in Fig. 1 may not be directly applied to STO.   However, the practical Φ_{STO} obtained here could be used as an index to determine the work function of Au and other materials on STO.   In addtion,_from a band scheme given by Dietz *et al.* [5] Φ_{STO} as the energy difference between the Fermi level and the vacuum level can be estimated as 6.0 eV.

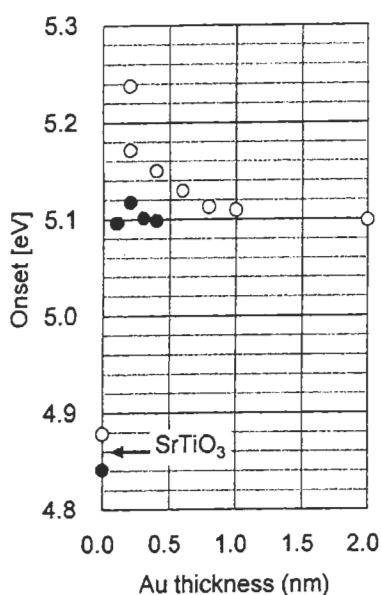
Figure 5. Work function change during Au deposition on SrTiO₃. ($\Phi_{Au} = 5.1$ eV [3]) Two different data sets are shown by open and filled circless

Work function of YBa₂Cu₃Oₓ at coevaporation mode

Figure. 6 shows the measured work function of growing YBCO film on the STO substrate at coevaporation mode in ozonic atmosphere. The substrate temperature estimated from the indication of an optical thermometer was ca. 600 C. The growth rate was 1.2 nm (= one unit cell along c-axis) per minute. Although the YBCO surface could be easily damaged by the electron beams, the strong oxidation effect of ozone can prevent the surface damage as evidenced by, for example, the stable streaky RHEED patterns during the film growth.
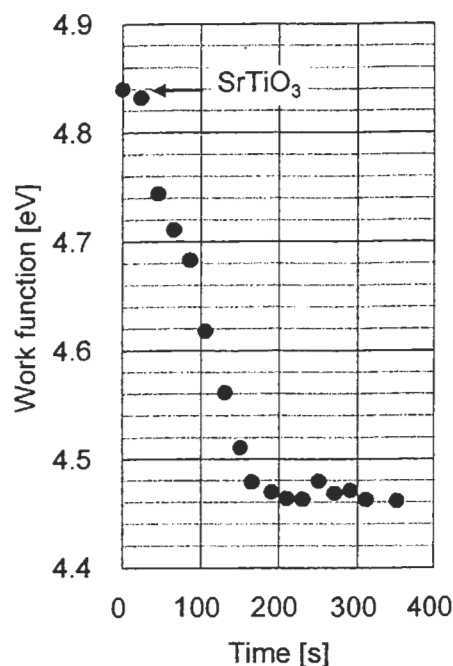

Figure 6. Work function change during YBCO film growth on SrTiO₃ at coevaporation mode.

The observed work function kept decreasing after one-unit growth till approximately three-unit layers growth.   The one possible reason for this is the effect of the structure relaxation of the ultrathin YBCO film because of the lattice mismatch between STO and YBCO.   The mismatch is 2.2% [6], which is sufficiently small to enable the hetero-epitaxial growth of YBCO on STO but may not be small enough to neglect the effect of the lattice relaxation.   Provided the initial work function, *i.e.*, Φ_{STO}, is 4.84 eV as in the graph, Φ_{YBCO} is found to be 4.46±0.04 eV.   Reported values for Φ_{YBCO} range from 4.0 eV to 6.1 eV [7a-7c] from which there is no good reason to choose the most probable value.

The film growth showed so-called *unit-by-unit* growth behavior in which the intensity of the specular spot in the streaky RHEED pattern oscillated with 1-minute period reflecting a cyclic change in the surface roughness, and the result in which the measured work function did not show any periodic change indicates that the top layer or at least the electronic structure of the film during the deposition remained the same.   The result, therefore, supports the direct formation of the YBCO units with an identical structure during the film growth.

Work function of YBa₂Cu₃Oₓ at sequential evaporation mode

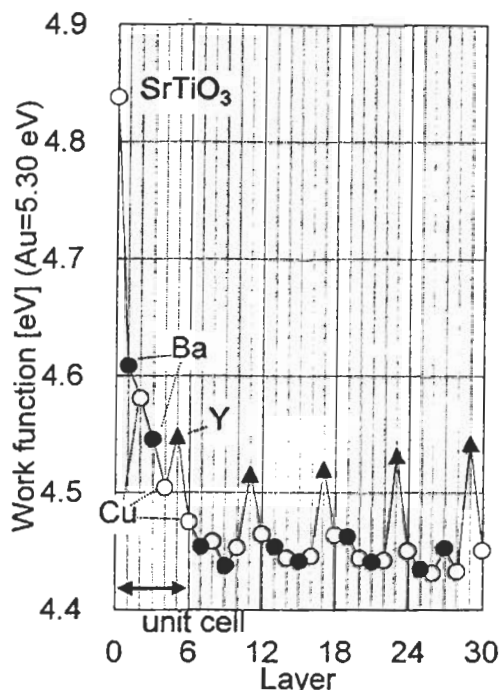The measured work function of growing

Figure 7. Work function change during YBCO film growth on SrTiO₃ at sequential evaporation mode starting with Ba.

YBCO film on the STO substrate at sequential evaporation mode is shown in Fig.7. The sequential of the metal deposition was Ba:Cu:Ba:Cu:Y:Cu:.. beginning with Ba so that the epitaxial film could be obtained. As in the previous report [1], the RHEED pattern was rather spotty throughout the film growth except for Y deposition in which the pattern suddenly turned streaky indicating the formation of a flat surface.

As seen in the graph in which Φ_{STO} is again fixed at 4.84 eV, the measured work function after evaporation of either Ba or Cu is 4.43 eV-4.46 eV except for the first unit, which is closed to the one at the coevaporation mode. The expitaxial YBCO growth in the *layer-by-layer* mode does not proceed for as much thickness as in the *unit-by-unit* mode probably because of instability of the intermediate oxides before the complete units are formed. Although Fig. 7 shows the work function change within a range of successful film growth, the gradual changes in the work function especially after Y deposition might be due to segregation of impurity oxides such as Y_2O_3 and BaO. As evidenced by the appearance of the streaky patterns in the RHEED screen [1], the completion of the YBCO units should occur only after evaporation of Y when the work function shows the distinct peaks above 4.5 eV. However, in our previous study

using the in-situ RHEED-AES, the signal intensity for a metal element always increased after the deposition of the element except for Y of which the signal could not be deconvoluted, whereas the signal intensity for each element kept constant in the coevaporation mode. Therefore, even though the structure of the YBCO films prepared by the two growth modes eventually becomes identical, the surface layer could differ in initial growth up to several unit layers resulting in the different work function values.

4. Conclusion

The relative work function of growing surface of $YBa_2Cu_3O_x$ films to gold were measured *in situ* using the energy shifts observed in reflection high energy electron diffraction beam excited secondary electron peaks. The measured work function of the growing surface in the coevaporation mode settled to a constant value, whereas that in the sequential evaporation mode showed distinct peaks every after Y evaporation reflecting the completion of the YBCO unit cell growth. The reason for the apparent difference in the work function change is not clear, but according to our previous RHEED-AES data the surface structure in the initial growth may differ in the two growth modes resulting in the different work function values.

5. References

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