Interface potential measurement with electron spectroscopic method

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The method of the interface potential measurement with electron spectroscopic techniques was presented for the interface between a metal and a ultra-thin material with a band gap. The work function measurement with UPS under bias voltage and binding energy measurement of film components give the information about the contact potential originating from a dipole layer at the interface. The examples of such measurement for two kinds of alumina film – NiAl(110) interface, one with an epitaxial alumina and the other with an amorphous one, were demonstrated. The work function and the binding energy of Al 2p and O 1s of two alumina films with almost same thickness were different. Other examples for Au/Pd/alumina/NiAl(110) and two kinds of $HfO_2/SiO_2/n$-Si were also demonstrated.

1. Introduction

The progressing technology toward nano-sized materials has made the interface between two different materials more and more important. Especially, the contacts between materials with different electric property, i.e., metal-semiconductor, metal-insulator and semiconductor-insulator attract great attention. Figure 1 shows schematic potential diagram of the contact between material-A (metal) and material-B (material with a band gap). Due to electron re-distribution caused by the contact, the Fermi level of the material-B will align with the Fermi level of the material-A (E_F). According to the energy alignment, the energy difference between E_F and the valence band (VB) or the conduction band (CB) is determined. Since the Fermi level position of materials with a band gap is not evident, the Fermi level alignment is to be experimentally determined. Especially when the thickness of material-B is thin or the material-B is a film, the Fermi level position may be different from that in the bulk material. To elucidate the Fermi level alignment with thin material-B, a combined technique of work function measurement by monitoring secondary electron cutoff (SC) with XPS core-level measurement is powerful.

2. The principle

Figure 2 illustrates the principle of work function (φ) measurement with secondary electron cutoff. When a light with $h\nu$ is irradiated on the surface, excited electrons come out to a vacuum. The lowest kinetic energy of electrons emitted is zero. The highest is $h\nu-\varphi$, since all the electrons have to get over the potential barrier of φ. Therefore, the energy of
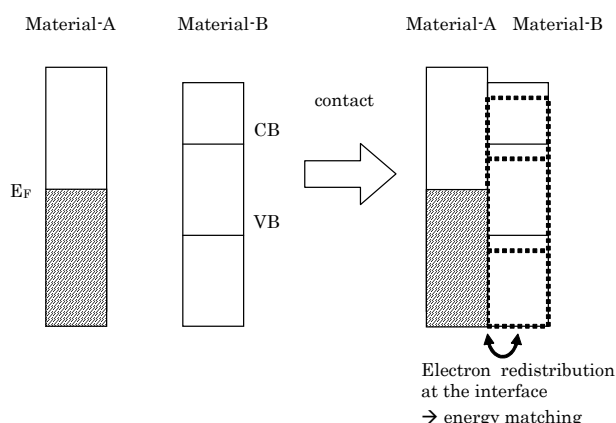

Fig.1 Schematic potential diagram of the contact between material-A (metal) and material-B (material with a band gap).

emitted electron ranges from zero to $h\nu-\varphi$. This is experimentally measured by electron spectroscopy while an appropriate negative bias voltage is applied to a specimen. The electrons with the highest kinetic energy have zero binding energy, which refers to the Fermi level of an instrument and does not shift due to work function change of a specimen. Therefore, the difference in work function among materials is observed by the shift of the secondary electron cutoff (SC) position. The potential diagram and schematic spectra in case of two materials in contact is shown in Fig.3. By observing the secondary electron cutoff, work function change is obtained. The measurement near the Fermi level gives information about the energy level position of valence band maximum (E_V) in the material-B.
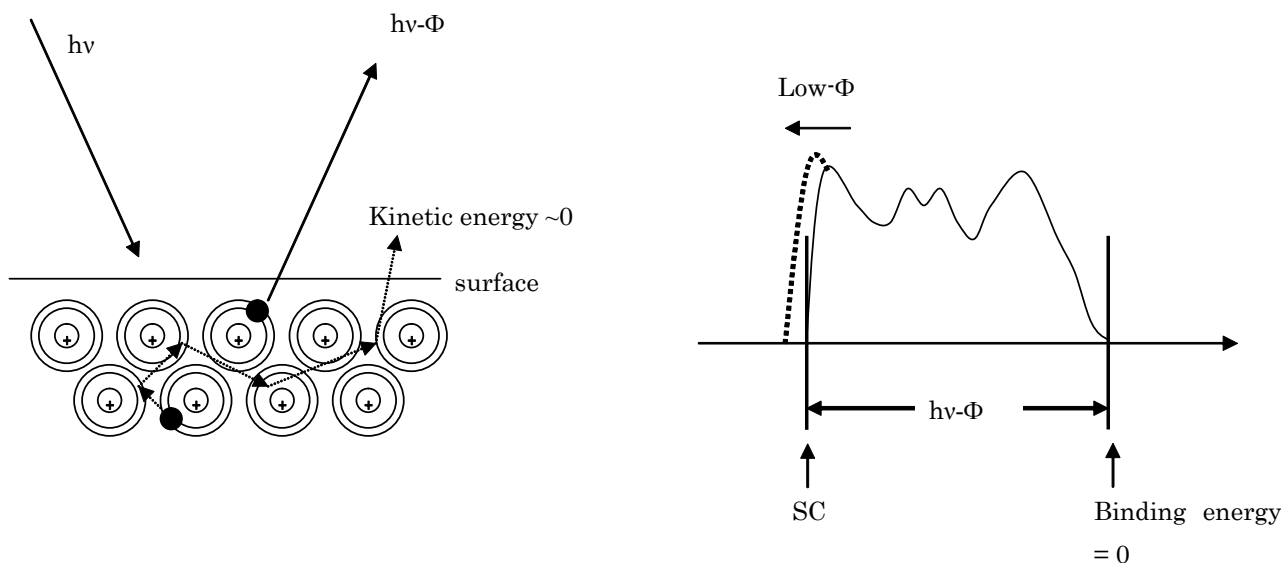
Fig.2 The schematics of the principle of work function (φ) measurement with secondary electron cutoff (SC) under a light (hν) irradiation.
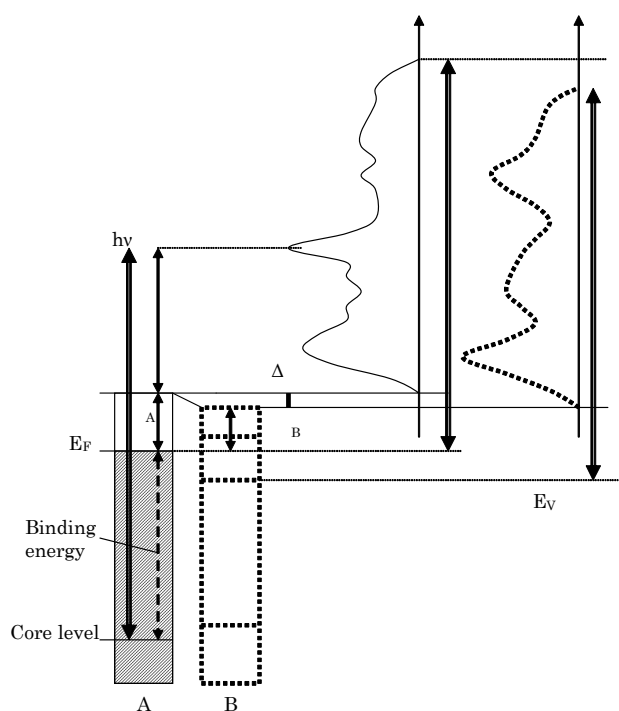
Fig.3 The potential diagram and schematic spectra in case of two materials in contact.

3. Example of the measurements

In this chapter, the examples of energy level determination by experiments are described. The positions of peaks were determined by the Gaussian fit of top 5% of the peaks and the cutoff position was determined by taking the middle point between zero and the maximum of the secondary electron peak. The precision of work function measurement using UPS was about 0.02 eV and that by Kelvin probe was 0.02 eV. Work function was measured by multi-techniques, UPS, XPS and Kelvin probe in this paper, because the absolute values of work function is obtained by UPS and the influence of photon irradiation can be eliminated by Kelvin probe measurement in addition to the work function change measurement with XPS.

The example of the potential measurement with XPS and UPS is demonstrated for the interface between NiAl(110) and an ultra-thin alumina film. In Fig.4 (a) and (b), O 1s and Al 2p spectra excited with Al Kα during the oxidation of NiAl(110) at 1020 K in vacuum are shown. The UPS spectra under – 10 V bias from the same specimen is shown in Fig. 4 (c). We knew that under this oxidation condition, epitaxial alumina film grew [1]. In these spectra, the binding energy shifts in O 1s, Al 2p(3+) and O 2p are observed. At the same time, the shifts in secondary electron cutoff (SC) are also observed in Fig. 4(c). The amount of these shifts depended on oxygen dosage, i.e., alumina thickness. By calculating alumina thickness for each oxygen dosage from XPS intensity, the energy shifts are plotted as a function of alumina thickness in Fig.5 (a). In the figure, work function change
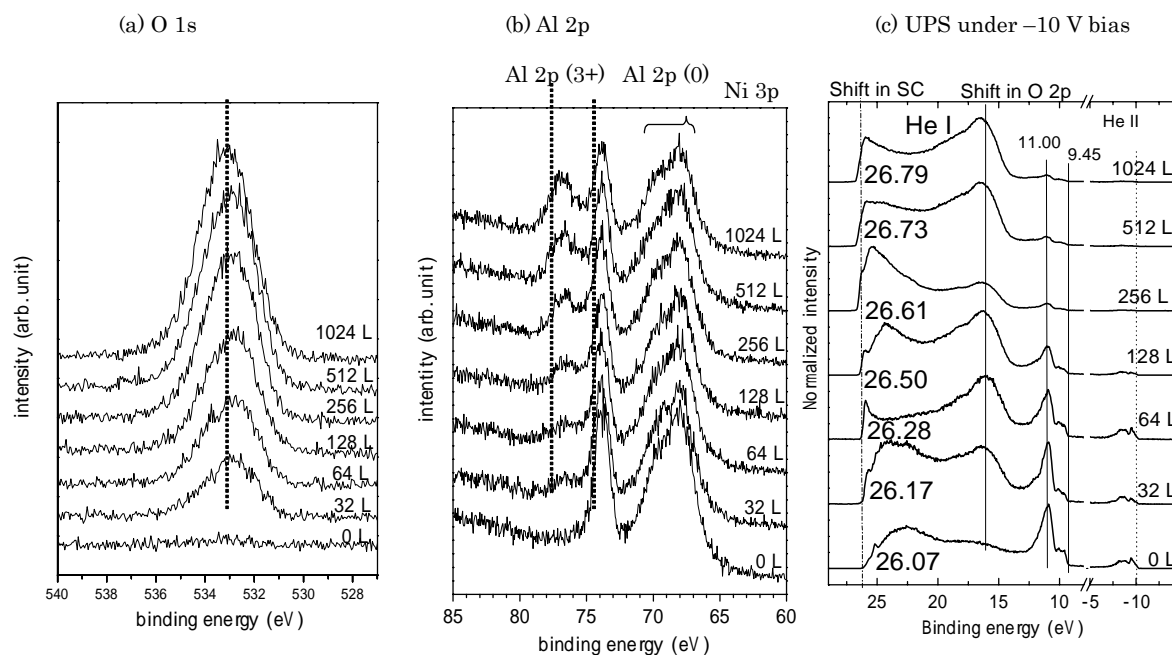
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Fig.4 The variation of O 1s (a) and Al 2p (b) spectra and UPS spectra under – 10 V bias (c) during the oxidation of NiAl(110) at 1020 K in vacuum.

measured by a Kelvin probe (KP) is also plotted. With the increase of the film thickness, work function decreased while the binding energy of Al 2p(3+) and O 1s increased (note the scales of the binding energy). The binding energy difference between O 1s and Al 2p was constant, suggesting that the chemical state of alumina was same for all the thickness. The shifts of O 1s and Al 2p were parallel, and they were parallel also with work function change. This implies that the shifts of O 1s and Al 2p were due to the potential change, but not chemical shifts.

By modifying the oxidation procedure (oxidation at 670 K), the growth of amorphous alumina film is also possible [2]. The similar measurement was carried out for the interface between NiAl(110) and the amorphous alumina film and the results are plotted in Fig.5 (b). With the increase of the film thickness, work function decreased, but the amount of the decrease was different from the epitaxial film. The binding energy of Al 2p (3+) increased but that of O 1s showed only a slight increase. In contrast to Fig.5(a), the binding energy difference between O 1s and Al 2p depended on the thickness, implying that the chemical state was not really that of stoichiometric alumina. The binding energy shift of Al 2p was almost parallel to the change of work function as in the case of the epitaxial film. The potential diagram in Fig.6 is deduced from those experimental results. In this diagram, the assumption is made that the Fermi level of the alumina films aligned to that of NiAl(110) (equilibrium real-

ized). The realization of the equilibrium seems to have been presumed without close examinations in many cases. However, it seems more probable that the Fermi level position of alumina is not aligned with that of NiAl(110) in our case, since the binding energy of Al 2p was different.

Similar experiment was performed for Au/Pd/alumina/ NiAl(110), where 2.7 nm of Pd film was first deposited on 0.8 nm epitaxial alumina grown on NiAl(110) followed by the deposition of 0.3 nm Au film on the Pd film [3]. Figure 7 illustrates the schematic potential diagram deduced from the experimental results, where the position of the Fermi levels were estimated by comparing the binding energy of Al $2p_{3/2}$ (3+), Pd $3d_{5/2}$ and Au $4f_{7/2}$ of the specimen with that of the bulk materials. The idea of the Fermi level misalignment sounds abnormal and is not studied well. However, dipole layer formation at the interface is a well-acknowledged idea and the observed energy level alignment is in relation with a dipole layer.

Another example is for the interface between silicon and an insulating layer, which is presented in Fig.8. In case where a semi-conductor like silicon is involved, the situation becomes more complicated because the biding energy shift caused by band bending also occurs. The Si 2p, O 1s and Hf 4f peaks for two specimens, (a) HfO_2(2nm) / SiO_2 / n-Si and (b) HfO_2(2nm) / Hf (1nm) / SiO_2 / n-Si were measured and analyzed. Both specimens were fabricated by sputter deposition of Hf, (a):under oxygen, and (b): without oxygen
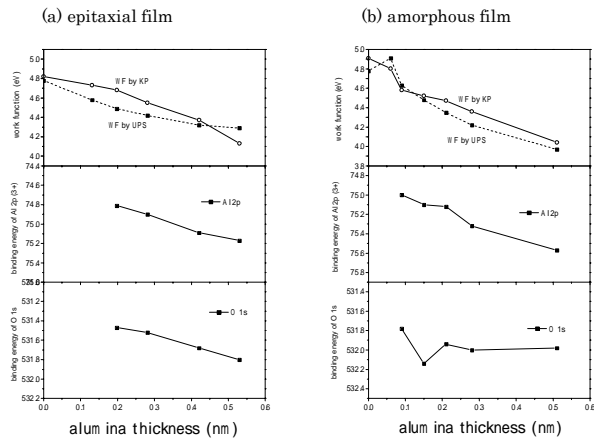
Fig.5 The binding energy shifts and work function change measured by SC and Kelvin probe (KP) plotted as a function of alumina thickness for (a) epitaxial and (b) amorphous alumina.
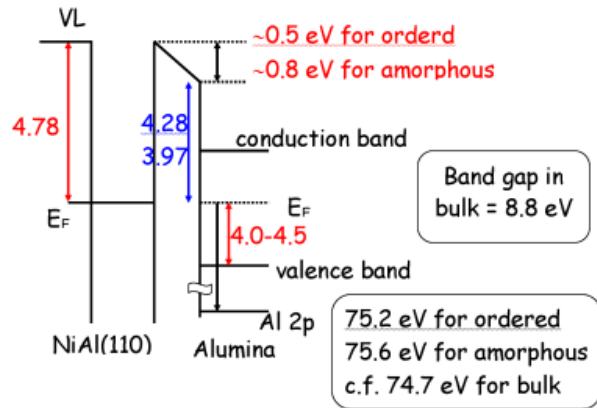

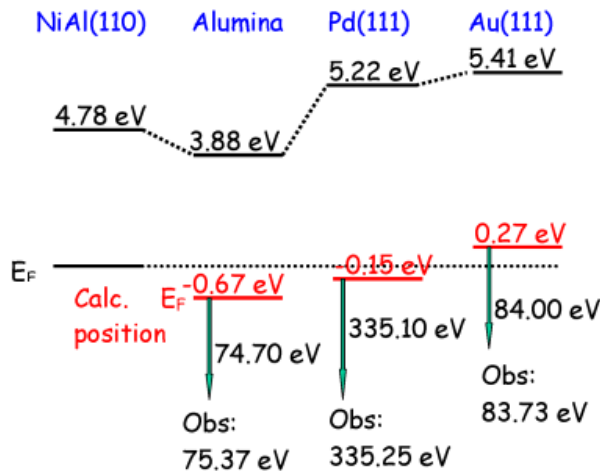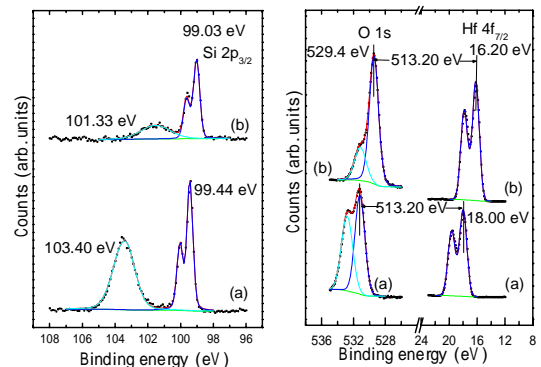Fig.6 The potential diagram deduced from the experimental results in Fig.5.

Fig.7 The experimentally obtained potential diagram of Au(0.3 nm) / Pd (2.7 nm) / alumina / NiAl(110).

first and then under oxygen. Due to the interface reaction, there was no metallic Hf at the interface but (a) has Si-rich and (b) Hf-rich HfSixOy at the interface. In this case, we observed the binding energy shift of Si $2p_{3/2}$, which exhibits the band bending caused by the contact. The detailed analysis and discussions are given elsewhere [4]. The deduced potential diagram shown in Fig.8 suggests that the position of valence band maximum (E_V) of HfO$_2$ with respect to the conduction maximum (E_C) of Si is interface dependent. If we assume the band gap of bulk value, the energy difference between E_V of Si and E_C of HfO$_2$ is also largely dependent on the interface.
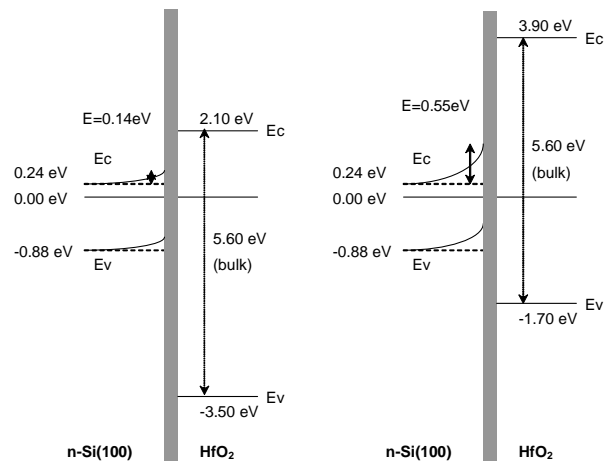

Fig.8 The experimental results for the interface between silicon and an insulating layer.

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4. Conclusion

The electron spectroscopic method to investigate the Fermi level alignment at the interface between materials with different electric property was presented. The experimental results on the interface between ultra-thin alumina films and NiAl(110) were shown. The work function change and binding energy shifts of Al 2p (3+) and O 1s showed parallel shifts in case of epitaxial alumina, which suggested that all the shifts were due to the interface potential. The similar experiments on the amorphous layer revealed that both the work function change and the binding energy shifts were different from the case of the epitaxial layer. It showed that both interface potential and stoichiometry was different from the epitaxial one. The study of the interface potential on Au/Pd/alumina/NiAl(110) implied that the Fermi level of Au/Pd layer doesn't match with that of NiAl(110) due to insulating property of alumina film. In case of HfO_2/SiO_2/n-Si with differently prepared HfO_2/SiO_2 interfaces, it was demonstrated that the Fermi level of HfO_2 film aligned differently with that of bulk n-Si when the interfaces were different. It was also shown that the amount of band bending of n-Si at the interfaces was greatly influenced by how the interfaces were prepared. The results presented here demonstrate that the photoelectron spectroscopy has a great potential for the investigation of the interface potential.

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