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Nondestructive In-Depth Profiling of Electronic Structures of Semiconductor Surfaces and Interfaces

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The demand for a good techinque to profile a in-depth electronic structure has increased more and more, as the thicknesses of the active layers in the electronic devices have become thinner. Low-energy electron energy loss spectroscopy (LEELS) seems to be the best method for that purpose, since the probing depth can be easily varied only by changing the primary electron energy in LEELS. Here we report on the first measurements of the LEELS spectra of Si(111) 7x7 and Si(100) 2x1 clean surfaces and a Si/SiO₂ interface, in which the primary electron energies have been changed systematically. It has been proved that LEELS is a powerful technique to investigate the in-depth variation of the electronic structures non-destructively.

I. Introduction

Recently the thickness of the active layers in the electronic devices has become thinner, and the demand for a good technique to profile the indepth electronic structures has increased more and Low-energy electron energy loss spectromore. scopy (LEELS) seems to be one of the most suitable method for that purpose, since the energy of primary electron and therefore the probing depth can be easily changed in LEELS. But so far there have been no systematic investigations on the usefulness of LEELS for in-depth profiling of electronic structures. Here we will report on the first measurements of the LEELS spectra of Si(111) 7x7 and Si(100) 2x1 clean surfaces, in which the primary electron energies are changed systematically to change the probing depth. We will also report on the elctronic structure of interface between Si and SiO_2 , which is one of the most important interface in the electronic devices.

The surface sensitivity and the depth resolution of electron spectroscopy are determined by the mean free path of the probing low energy electrons. The solid line in Fig. 1 shows the typical energy dependence of the mean free path of the electrons in solids, which shows weak dependence on the kinds of materials [1]. It reaches the minimum value at about 50-60 eV, above that it increases monotonously with the electron energy.

The probing electrons in the LEELS measurements penetrate into the specimen surface, are backscattered in the specimen and come out to the vacuum, and thus traverse the surface region twice. In addition to that the cylindrical mirror analyser (CMA) usually used in the LEELS measurement collects electrons incomming at the angle of 42.3° from the CMA axis, which means that electrons passing through the sample to that oblique direction are collected. Thus the effective mean free path is shortened in LEELS, resulting in better surface sensitivity and depth resolution. The broken and dash-dotted lines in Fig. 1 show the effective mean free path for the loss energy of 10 eV and 100 eV, respectively. Then one can change the proving depth from about 2 Å to 10 Å by varying the primary electron energy from 50 eV to 2000 eV.



Fig. 1. Mean free path of electrons in solids as a function of energy.

II. Experimental

In order to see the depedence of the LEELS spectrum on the primary elctron energy in detail, it is essential to use an energy analyser having a constant energy resolution in the whole energy range of measurment. We have met this requirement by using a double pass CMA (PHI 15-255G) in the retarding mode, with which the constant energy resolution of 0.5 eV has been obtained in the entire energy range from 20 eV to 2000 eV.

When the primary electron energy is larger than 1000 eV, only a small numbers of electrons are backscattered. Thus it is needed to increase the sensitivity of the LEELS measurement. High sensitive measurement has been realized by using a pulse count detection and repeating the energy sweep and accumulating the counts to improve the SN ratio. The second-derivative spectra have been obtained by the numerical differentiation of the measured spectra after measurements [2]. The increase in the sensitivity is also helpful to decrease the primary electron beam current, whereby the irradiation effect of the primary electrons on the specimen surface is kept as small as possible.

III. Results and Dicussions

3.1 2H-MoS2

The instrumental dependence on the primary electron energy have been checked by measuring the LEELS spectra of a clean cleaved face of 2H-MoS₂, which has a layered crystal structure and no dangl-Then it is ing bonds on its cleaved surface [3]. expected that the electronic structure is nearly the same from the top surface to the bulk. Fig. 2 shows the observed LEELS spectra of 2H-MoS₂ for Here the peaks varios primary electon energies. $E_1 - E_4$ arise from the interband electonic transitions, and the peaks $h\omega_{_{
m D}}$ are due to the partial plasmon excitation. The peak Ex comes from the ex-As is seen in the figure, citonic transition. the observed spectra are essentially the same for the primary electron energy from 100 eV to 1600 eV except the change in the magnitude of the peak Ex. This results strongly indicates that the constancy of the present measuring system is well acceptable in the whole measuring energy range, as well as



Fig. 2. Primary electron energy dependence of LEELS specta of a cleaved face of 2H-MoS₂.



Fig. 3. Primary electron energy dependence of LEELS spectra of a Si(111) 7x7 surface.



Fig. 4. Plot of intensities of surface-related peaks normalized to the bulk peak E₂.

that the electronic structure of $\rm 2H-MoS_2$ is almost the same from the surface to the bulk.

3.2 Si(111) 7x7 and Si(100) 2x1 surfaces

The LEELS spectra for clean silicon surfaces have shown large dependence on the primary electron energy. The surfaces of Si(111) and Si (100) wafers were cleaned by flushing with electron beam bombardment just before measurements. All measurements were done under 8 x 10^{-9} Pa. Surface cleanness was checked by Auger electron spectroscopy, and no trace of contamination was observed. The surface reconstruction was checked by RHEED.

Fig. 3 shows the LEELS spectra of Si(111) 7x7 surface for various primary electron energies. Here the peaks labeled as $h\omega_{\rm p}$ and $h\omega_{\rm s}$ come from the bulk and surface plasmon excitation, respectively. The peaks E_1 and E_2 are due to interband electronic transition, while peaks S_1 , S_2 and S_3 are related to the intrinsic surface states and their intensities decrease with the increase in the primary electron energy. Fig. 4 shows the dependence of the surface related peaks normalized to the bulk peak E_2 on the primary electron energy The intensity of the lowest loss peak at 1.9 eV decreases drastically with the increase in the primary electron energy. This peak is considered to arise from the electronic transition between the filled back bond state and the empty dangling bond state [4]. The present result clearly indicates that the S1 peak relates directly to the surface dangling bond states localized on the top surface.

The normalized intensities of the peaks S_2 and S_3 , on the other hand, show the maxima at the primary electron energy of about 600 eV and 400 eV, respectively, indicating that those peaks are



Fig. 5. Plot of intensities of surface-related peaks normalized to the bulk peak E_2 .

related to the surface states localized in the deeper portion. There are two possibilities for the origin of these peaks. One is the electronic transition between the back bond and the dangling bond states [5], the other is the one between the back bond and the bulk conduction band states [6]. The present result is in favour of the latter origin.

Similar results were obtained for Si(100) 2x1 clean surface. Fig. 5 shows the primary electron energy dependences of surface related peaks normalized to the bulk peak E_2 . The normalized intensity of peak S_1 decreases drasticaly with the increase in the primary energy, revealing that it arises from the electronic transition between the back bond to the dangling bond states. Peak S_3 is considered to come from the electronic transition band states similarly as the case of Si (111) surface. Peaks S_2 and S_2' are too weak to obtain definite conclusions.

3.3 Si/SiO₂ interface

The above technique has been also applied to the study of the electronic structure at the interface between a very thin layer of SiO_2 film and silicon. The thin layer of SiO_2 was grown by thermal oxidation of clean silicon surface at 800



Fig. 6. Primary electron energy dependence of Si(2p) core electron excitation spectra of SiO₂ on Si.

°C for 30 min under 1×10^{-2} Pa oxygen atmospher, of which thickness has been estimated as about 10 Å from the dependence of the observed LEELS spectra on the primary electron energy [7].

There are a few reports on the primary electron energy depedence of the LEELS spectra of a Si/ SiO₂ interface in the interband transition region Such collective excitation as interface [7-9]. plasmon, however, contributes to the spectra in that energy region, and it makes difficult to get definite informations on the interface electronic The spectra in the core electron exstructures. citation region are free from those interference, and LEELS spectra of Si(2p) core electron excitation region have been measured for the first time with varying the primary electron energy. Fig. 6 shows the primary electron energy dependence of the Si(2p) core electron excitation spectra of the prepared Si/SiO2 interface and those of clean surfaces of single crystalline silicon and SiO₂. As is seen in the figure, the spectrum changes gradually from that of SiO₂ to that of pure silicon with the increases in the primary electron energy The effect of the interand the probing depth. facial states seems to appear around 800 eV, which is about the middle of energies giving the two ex-Fig. 7 shows the subtracting protreme spectra. cess of the pure silicon (dash-dotted line) and SiO₂ (broken line) spectra from the spectrum ob-No distinct structure is seen served at 800 eV. in the resultant curve (c), indicating that the observed spectrum can be synthesized with mere superposition of pure silicon and SiO₂ spectra. This means that the interface between SiO₂ an silicon is very abrupt and that there is almost no intermediate layer at the interface. Even if it exists, its thickness may be one or two atomic layers.

In conclusion LEELS has been proved to be a powerful and non-destructive method for the indepth investigation of electronic structures. In principle its depth resolution is the best among the various electron spectrosopies and can be made as short as 2 Å. This technique seems to be useful especially to study the electronic structure of the interface beneath the surface.



Fig. 7. Decomposition of the LEELS spectrum of SiO₂ on Si for Ep=800eV.

References

- [1] G. Ertl and J. Kipper : Low Energy Electrons and Surface Chemistry (Verlag Chemie, Weinhelm 1974)
- [2] A. Koma and K. Yoshimura : Jpn. J. Appl. Phys. 22, (1983) L173.
- [3] A. Koma and K. Enari : Proc. 14th Intern. Conf Phys. Semiconductors, Edinburgh, 1978, p. 895.
- [4] J.E. Demuth, B.N.J. Person, and A.J. Shell-Solokin : Phys. Rev. Lett. <u>51</u>, (1984) 2214.
- [5] A. Koma, R. Ludeke : Surf. Sci. <u>55</u>, (1976) 735.
- [6] J. E. Rowe and H. Ibach : Phys. Rev. Lett. <u>31</u> (1973) 102.
- [7] T. Ito, M. Iwami, and A. Hiraki : J. Pys. Soc. Jpn. 50, (1981) 2704.
- [8] T. Ito, M. Iwami, and A. Hiraki : Solid State Commun. 36 (1980) 695.
- [9] T. Ito, M. Iwami, and A. Hiraki : Proc. 12th Conf. on Solid State Devices, Tokyo, 1980 (Jpn. J. Appl. Phys. 20 (1981) Suppl. <u>20-1</u>) p.249.