Extended Abstracts of the 21st Conference on Solid State Devices and Materials, Tokyo, 1989, pp. 405-408

A Non-Destructive Surface and Interface Study of Very-Thin-Film/Substrate Contact Systems Using Soft X-ray Spectroscopy

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A non-destructive surface and interface structure analysis is successfully carried out using soft x-ray spectroscopy(SXS) method for a very-thin-layer /Si(substrate) hetero-contact contact system. The method is based on the fact that the Si-L_{2,3} valence band SXS spectrum of a Si-compound shows a clear difference from that of Si crystal. Also is utilized the fact that a soft x-ray production depth increases with increasing an incident electron energy. Valence band electronic structure is also discussed.

1. Introduction

The increment of the integration of electronic devices has made the packing density increased, which, in turn, requires preparation of very thin layers with enough precision, where hetero-interfaces must also be fabricated in a well controlled manner. This can be accomplished with having a proper analytical tool which is able to explore, hopefully non-destructively, the compositional and/or the electronic structure.

When energetic electrons are impinging onto a material, photons are emitted to give informations on either electronic or structural properties. Among wide varieties of photon emissions, soft x-ray spectroscopy (SXS) is a powerful tool to have information of electronic structure of materials, where the photon energy is less than ~1 keV. One excellent characteristic of SXS is the fact that the method is especially suitable for the determination of the electronic structure of valence band, because a core level involved in the soft x-ray emission has little wave number dependence.¹⁾

A transition-metal-silicide is one of the most important materials used in semiconductor devices and has long attracted attention for its characteristics, e.g., its refractory nature and its electrical conductivity.², ³) In spite of the difference in their nature, such as lattice constant, between a grown material and Si, the epitaxial growth of a material on a Si substrate has successfully been reported in several systems, e.g., NiSi₂ on Si single crystal.

Considering the situation that a nondestructive characterization method will play important roles in the course of electronic device fabrication, we have been studying a Si-compound(thin film)/Si(sub strate) system using the SXS method with an electron excitation. In this work, electronic and structural properties are studied for transition-metal-silicide/Si contacts, where a non-destructive depth profiling is carried out utilizing an energy dependence of an x-ray production depth of an energetic electron in a solid.^{4, 5)}

2. Experimental

Transition metal/Si contacts were prepared by a solid phase epitaxy. First, transition metal, e.g., Ni, film with thickness of 10-100 nm was deposited on a Si substrate. Then the specimen was heat treated in an electric furnace under $N_2 + H_2$ gas flow at an appropriate temperature, e.g., about 800°C for the case of a thick film epitaxial growth of NiSi₂ on Si substrate. Growth of a silicide with an expected composition and/or a crystal structure was ascertained by an x-ray diffraction and an XMA (x-ray microanalysis).

SXS experiments were carried out in a vacuum chamber with an x-ray tube and an x-ray spectrometer in an ambient pressure of $\sim 10^{-6}$ Pa during analysis, where the latter was connected through a fine slit. The width of the slit could be varied and was kept 30 µm in the present study. Specimens to be analyzed were put on the Henke-type x-ray tube which was used to prevent the specimen on the anode from contamination to be given by a tungsten filament, i.e., an electron source. Either the incident angle of the electron beam or the take-off angle of emitted x rays was at 90° to the specimen surface. Energies of incident electrons, E_p, were varied between 0.85 and 4 keV. The electron flux was ~ 1 mA on a region of \sim 0.3 cm². Specimens were kept at room temperature by water cooling. Soft x-ray emission spectra were obtained with a grazing incidence spectrometer, where a grating with a radius of 2 m and 1200 grooves/mm was used. An energy resolution of the spectrometer is better than 0.6 eV. Details of the SXS experiments are given elsewhere.⁶⁾

3. Results and Discussion

Si-L2.3 soft x-ray emission band spectra are shown in Fig. 1 for a NiSi2 single crystal at different primary electron energies, E_n's. It should be noted that the Si L2.3 spectrum reflects a valence band density of state(DOS) with s- and d-symmetry due to the selection rule for an electron transition to induce a photon emission. The spectra of Fig. 1 have following characteristics: Both of them are almost the same in spectral shapes except for details. Each spectrum is composed of a broad peak at ~ 91 eV, a terrace at 94-98 eV and a sharp peak at ~100 eV. The peak at ~100 eV is constructed by two peaks separated by 0.6 eV. The strong and sharp peak at ~ 100 eV can be concluded to correspond to the valence band DOS (density of state) with s- or d-symmetry from the discussion above.⁷⁾ Indeed, the signal is due to the Si-Ni bond formation, because such a signal cannot be seen in the spectrum for a Si single crystal as will be



Fig. 1 Si $L_{2,3}$ soft x-ray emission band spectra for a NiSi₂ single crystal at $E_p = 4$ (a) and 2 keV (b).

shown below.

Spectra for a Si single crystal is shown in Fig. 2 at different E_{p} 's. In this case, features to be noted are as follows: Spectra for different Ep's are almost identical. Each spectrum has a peak at ~ 89 eV, the one at ~ 92 eV and a shoulder at ~ 96 eV. At a glance, it is clear that there is a very big difference between the spectra of Fig. 1 and those of Fig. 2. Differences to be noted at least is spectral shapes at ~ 90 eV and at ~ 100 eV. The former is broad one in NiSi₂ single crystal and double peaked one in Si single crystal. The spectral shape of NiSi $_2$ at ~ 100 eV is sharp and double peaked with an energy separation of \sim 0.6 eV, and is structureless in the one of Si single crystal. Such kind of clear differences in Si-signal are hard to be seen in other electron spectroscopies which can give information about the electronic structure of Si, such as the conventional first derivative spectra, dN(E)/dE, of the Si(LVV) Auger signal. Although a careful examination



Fig. 2 Si $L_{2,3}$ soft x-ray emission band spectra for a Si single crystal at $E_p = 4$ (a) and 1 keV (b).

of Auger spectra yields differences among the spectra, we cannot tune the sampling depth in the Auger experiment, because the kinetic energy (E_k) of a given Auger electron is almost constant, e.g., the Si(LVV) Auger signal is at $E_k \sim 90$ eV, which is independent of E_p 's.

These characteristics of the SXS spectra, in combination with energetic electrons as a source of excitation of photons, can be used for a non-destructive analysis of Sicompound(thin film)/Si(substrate) contact systems as has been proposed previously.⁸) At $E_p > 100 \text{ eV}$, an x-ray production depth of an energetic electron increases with increasing E_p to reach deep inside of a solid.^{4,5}) Therefore, the depth probed in this experiment can be tuned by selecting simply proper electron energy.

An E_p dependence of the Si L_{2.3} emission band spectrum of a NiSi₂/Si(111) specimen is as follows. At $E_p = 0.85$ keV, the spectrum is considered to be almost the same as the one of NiSi2 single crystal. Then the intensity of the soft X-ray emission band spectrum becomes to have an increased contribution of the lower (~ 89 eV) and the higher (\sim 92 eV) energy components with increasing E_p. In the same manner, the sharp peak at ~100 eV becomes less clear with increasing E_p . Finally at $E_p = 4$ keV, the Si-L_{2.3} soft x-ray emission band spectrum becomes quite similar to the one of pure Si crystal, which is considered to correspond to the signal mainly from the substrate Si(111). At intermediate Ep's, Si-L2.3 spectra look like a mixture of the one of NiSi2 single crystal and that of crystalline Si. Features of an SXS spectrum of a NiSi₂/ Si(111) specimen at an incident electron energy(E_p) of 2 keV, for example, are as follows: The signal at $\sim 90 \text{ eV}$ is double peaked, where the energy separation between

the two peaks is less than that of a Si single crystal. The line at ~ 100 eV is less intense compared with that of a NiSi₂ single crystal.⁹

Next, we have tried to get composed spectra by superposing the experimental spectrum of a Si single crystal to that of a NiSi2 single crystal, where experimental spectra are those at $E_p = 4$ keV of Figs. 1 and 2. The superposition is carried out by changing x-value in (1-x)NiSi₂ + xSi. A1though there is a little change in spectral shape in the bulk NiSi2 single crystal with E_p , the spectral features of the Si-L_{2.3} emission band at \sim 90 and \sim 100 eV are almost unchanged at different E_n's. The feature to be noted is the fact that $Si-L_{2,3}$ spectra have a broad and a single-peakedstructure at \sim 91 eV and a sharp peak at \sim 100 eV, see Fig. 1, even when E_p is changed between 0.85 and 4 keV. On the other hand. the spectrum of crystalline Si has a doublepeaked-structure at ~ 90 eV, i.e., ~ 89 and \sim 92 eV, and no peak at \sim 100 eV at every $E_{p}(0.85 \sim 4 \text{ keV})$ adopted, e.g., Fig. 2. Therefore, this kind of spectrum composition can be expected to give an structural information for the NiSi₂/Si(111) specimen studied with the help of an x-ray production depth of an energetic electrons in solid materials.

5. Summary

It should be emphasized that the new application of the SXS method is very powerful to examine an ultra-thin-film(< several tens of nm)/substrate contact system without adopting any destructive tool. In the present case, we have successfully separated a signal due to Si-atoms in the surface Sicompound region from that of the Si substrate. Also, we can clarify the chemical bonding state of an element in a film studied using soft x-ray spectra.

Acknowledgments

The authors would like to thank Dr. H.Taguch for his help in an x-ray diffraction experiment. This work is partly supported by the Science Research Promotion Fund of Japan Private School Foundation. Thanks are also due to the Scientific Research Grant-in Aid #01650005 for Special Project Research on "Metal-Semiconductor Contacts", from the Ministry of Education, Science and Culture.

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