INVESTIGATION OF DENSITY-OF-STATES IN TISI AND TISi2 COMPOUNDS

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The electronic structure of TiSi and TiSi₂ was investigated by means of the energy distribution of photoelectrons emitted from the valence band and core levels. The Ti *d*-states are dominant at the Fermi level, the Si *s*-states of both TiSi and TiSi₂ were shifted to lower binding energy. The Si *p*-states are modified having peaks at binding energies 2.7 and 4.2 eV for TiSi₂ and 2.8 eV for TiSi but their intensities differ widely. The Si *sp*-states were not detectable for TiSi₂ nor was the core level shift for TiSi₂.

INTRODUCTION

A LARGE VARIETY of the metal silicide systems have been developed for the application in the VLSI microelectronics. The properties (resistivity, chemical bonding etc.) of the different compounds are strictly related to the electronic structure of silicides which have been investigated extensively by electron spectroscopy, e.g. UPS and XPS, the main target materials being the noble and transition metal silicides. The general features of the density-of-states of the transition metal silicides are the unbonded d-band of the metal and the s-level of silicon. The metal-silicon interaction is concentrated on Si pand transition metal d-hybridization [1-5]. So far only DOS for TiSi₂ indicating an Si p and Ti d-hybridization near the Fermi edge has been reported [6].

In the present paper we are concerned with the Ti-Si system, especially, with $TiSi_2$ and TiSi, for which comprehensive UPS and XPS data are first given here.

EXPERIMENTAL

TiSi and TiSi₂ films were prepared by solid phase reaction between the evaporated Ti layer (20 nm thick) and the Si $\langle 1 1 1 \rangle$ substrate. Evaporation was carried out at 10⁻⁸ Pa, and *in situ* annealing was performed at the same pressure. TiSi and TiSi₂ were respectively formed at 550 and 700°C from the same type of titanium and silicon structure. This process was necessary for the preparation of an oxygen-free silicide layer. The compounds of the samples were identified by X-ray dif-



Fig. 1. Photoelectron energy distribution curves of UPS for TiSi and $TiSi_2$.

fraction with a Philips Vertical diffractometer. X-ray data showed pure polycrystalline TiSi and TiSi₂ phases. The UPS and XPS measurements were carried out by a Kratos ES-300 type electron spectrometer at 10^{-8} Pa with a resolution of 0.2 and 0.7 eV for UPS and XPS, respectively. The samples were cleaned by Ar⁺ etching immediately before the measurement. The HeI and AI K α lines were used for excitation. During the measure-



Fig. 2. UPS spectra in 0-5 eV binding energy range for $TiSi_2$, TiSi, Ti and Si.

ments the intensity of the HeI source was held constant. The investigations were performed by a hemispherical analyser in the constant relative energy resolution $(\Delta E/E)$ mode. Evaporated Ti films of 200 nm and Si $\langle 1 1 \rangle$ wafer bombarded by 2 keV Ar⁺ – during the etching – were used as references for the measurements.

RESULTS AND DISCUSSION

The representative valence band emissions from TiSi and TiSi₂ are shown in Fig. 1. It is seen that the general shapes of these curves are similar. Three different regions of the spectrum could be distinguished, viz in the 0-2, 2-5 and 8-10 eV energy ranges.

In the first region there is a large peak at the Fermi level in TiSi and TiSi₂. The photoelectron intensity at E_F , i.e. the density-of-states is larger for TiSi₂ than for TiSi. These data may be correlated with the lower resistance of TiSi₂ vs TiSi [10].



Fig. 3. Energy distribution curves of photoelectrons emitted from the 7-10 eV energy region of the valence band of TiSi, TiSi₂ and Si.

The 2-5 eV energy range shows a double peak for TiSi₂, but only one peak for TiSi. In the third energy region (8-10 eV) in which the silicon s-valence band emission is included, a definite peak is visible for both compounds. No significant structure is observable in the 5-8 eV binding energy region for the two compounds if the oxygen signal (1s) is less than 3 per cent of the Si 2p-emission; otherwise, the emission in this energy range is due to the oxygen contamination on TiSi and TiSi₂. It is concluded that there are no electron states for TiSi and TiSi₂ compounds within the 5-8 eV energy range which belongs to the silicon sp-valence band. The 0-5 eV binding energy regions for TiSi, TiSi₂ and Si are



Fig. 4. Si $2P^{3/2}$ emission of Si and TiSi₂.

detailed in Figs. 2 and 3, respectively. It is seen that our photoemission data for Ti and Si are in agreement with the literature on polycrystalline sample [7, 8]. The peaks at the Fermi level for TiSi and TiSi₂ are similar to Ti *d*-emission but they show definite differences, too. The FWHM of these peaks are 1.3, 0.8 and 0.6 eV for Ti, TiSi and in TiSi₂, respectively. A possible explanation of these results is that the chemical bonding of Ti and Si as well as Ti-Ti distance in TiSi and TiSi₂ vs Ti, are changed.

Although the 2-5 eV energy region coincides with the Si p and the second d-peak of Ti in the valence band, the EDCs for TiSi and TiSi₂ differ from the photoemission data of polycrystalline Si and Ti. By comparing these data with those calculated for the electronic structure of other TM silides [4, 5] one may suggest that the A and B peaks as well as some modification of the d-states result from the hybridization. The difference between the spectrum of TiSi and TiSi₂ can be understood by assuming that the A, B peaks mainly result from the Si p-states and partly from the difference in the respective crystal structure [11].

According to Fig. 3, the Si s-band is shifted to lower binding energies which are 9.6, 9.3 and 9.1 eV for Si, TiSi and TiSi₂, respectively. The shape of the peaks is unchanged which indicates that the silicon "s" state in the valence band does not interact wich the *d*-orbitals of titanium. These shifts are explainable by charge transfer in TiSi and TiSi₂. This charge transfer, however, cannot be supported by the XPS data presented in Fig. 4, for Si 2p 3/2 emission in TiSi₂ and Si. The same was observed for Ti 2p 1/2 and 2p 3/2 levels in TiSi₂ and Ti.

These data indicate that the 0.4-0.5 eV core level shift estimated from the UPS data, it not confirmed by the XPS results thereby showing that the Si s-level-shift in the valence band is not explainable by charge transfer alone. Our suggestion for this effect is that the sp^3 hybridization of Si have been modified by Ti-Si bonding.

CONCLUSIONS

The density-of-states in the valence band of TiSi and TiSi₂ are different from each other and from Ti and Si as well. Near to the Fermi level peaks were detected for TiSi and TiSi₂. These peaks are derived from the Ti d-band but the FWHM and maximum of these peaks are different for TiSi, TiSi₂ and Ti showing that the d-states are different.

In TiSi₂ and TiSi, the peaks which are detectable at 1.7, 4.4 and 2.8 eV, respectively, originate from the Si 2p and Ti 3d hybridization. The silicon *s*-state in the valence band is shifted to smaller binding energy in TiSi and TiSi₂ compared with pure Si. This can not be interpreted in terms of the charge transfer since corresponding shift are not found for the core level electrons.

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