Chemical Shift at Interface for Silicides

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We investigated the natures of chemical bond at silicide/silicon interfaces for four silicide films ($CoSi_2$, $NiSi_2$, $TiSi_2$ and WSi) using X-ray photoelectron spectroscopy (XPS), with the purpose of getting insight on the nature of silicide/silicon interface. In the case of $CoSi_2$ and $NiSi_2$, the difference between XPS binding energy of metal and silicon peaks increased at silicide/silicon interfaces, whereas the difference for $TiSi_2$ and WSi decreased. The XPS binding energy differences between metal and silicon peaks before and after interfaces had good correlation with work function of metal, and relevance to Schottky barrier height at interface.

1. Introduction

Transition metal silicides, which are attractive materials for applications in electronic and optoelectronic devices, have been intensively studied during the past few years [1-5]. Recently, they are widely used in very large-scale integration circuit (VLSI) as gate electrodes, Schottky barriers, interconnects and ohmic contacts [6-8]. It is very interesting that we investigated the silicide/silicon interface, since there is a Schottky barrier by the contact between silicon and metal near interface [9-11] and electronic property is directly affected by nature of interface [12-13].

In this study, with the purpose of getting insight on the nature of silicide/silicon interface, we measured the binding energy of metal and silicon peaks at interfaces for four silicide films ($CoSi_2$, $NiSi_2$, $TiSi_2$ and WSi) using X-ray photoelectron spectroscopy (XPS), and investigated the natures of chemical bond at the interfaces.

2. Experimental

The silicide films ($CoSi_2$, $NiSi_2$, $TiSi_2$ and WSi) which were deposited on n-type Si (100) wafers using co-sputtering were supplied by Surface Analysis Society of Japan (SASJ). The thicknesses of all samples were about 200nm, and the crystal structures of them were poly crystal for $NiSi_2$, and amorphous for other sample. The other detailed information about their composition and so on, were described in reference 14. All samples were mounted on a stainless platen with conducting double sides tape. We carried out the XPS measurement while ion sputtering was carried out, and then investigated the natures of chemical bond at silicide/silicon interfaces. The experimental conditions of sputtering and XPS measurements are shown in Table 1.

Table 1 The Experimental conditions of (a) sputtering and (b) XPS measurements.

(a) Sputtering	
Ion Species	Ar^+
Ion Energy	0.5 ～ 4keV
Raster Size	3×3 mm^2
Ion Incidence Angle	45°

(b) XPS measurements	
Instrument	Perkin-Elmer Quantum-2000
X-ray Source	AlK_α (1486.6 eV)
Base Pressure	< 8×10^{-9} Torr
Take off Angle	45°
Acquisition	Pass Energy : 23.50 eV Step size : 0.05 eV
Resolution	0.66eV ($Ag3d_{5/2}$)

3.Results and discussion

Fig.1 and Fig.2 show the XPS binding energy and full width at half maximum (FWHM) of (a) metal and (b) silicon peaks at silicide/silicon interfaces of $CoSi_2$ and $TiSi_2$ films for 0.5keV ion sputtering, respectively. Here, the interface was defined as a middle point of 84% and 16% intensities in depth profile. The XPS binding energy of metal and silicon peaks for $CoSi_2$ increased and decreased at silicide/silicon

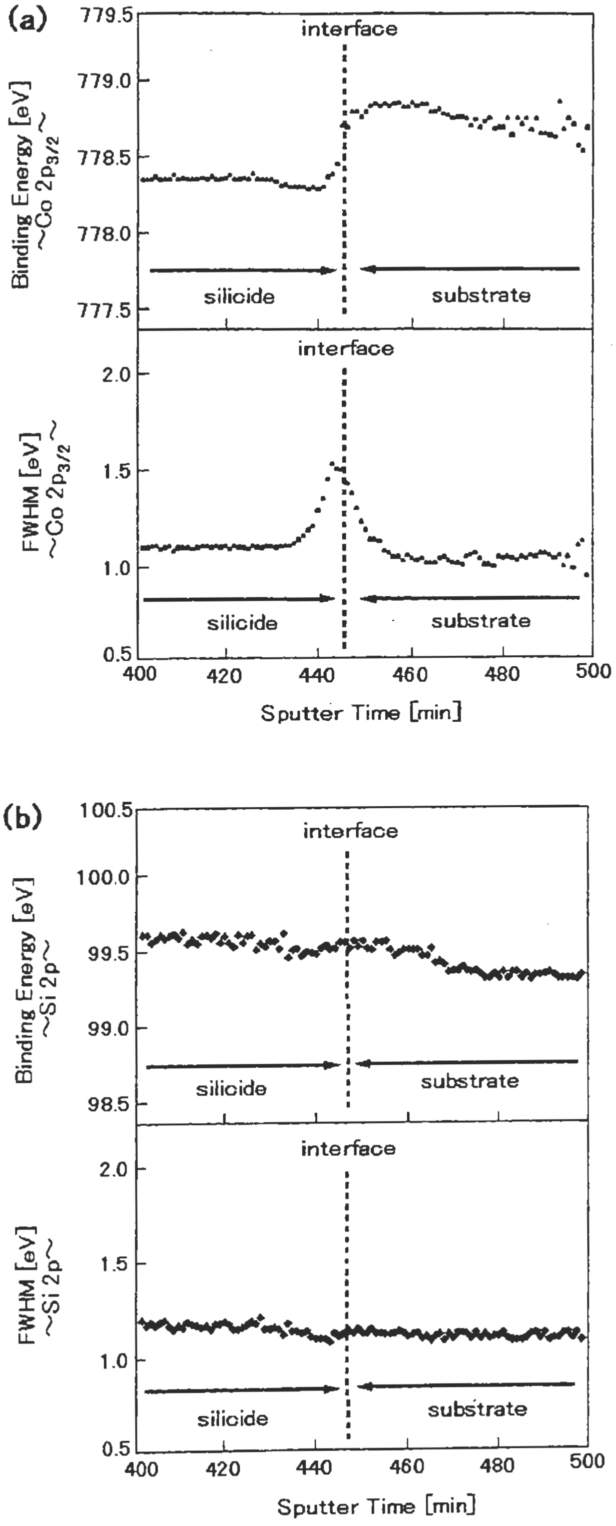

Fig.1 The XPS binding energy and full width at half maximum (FWHM) of (a) metal and (b) silicon peaks at silicide/silicon interfaces of $CoSi_2$ film for 0.5keV ion sputtering.

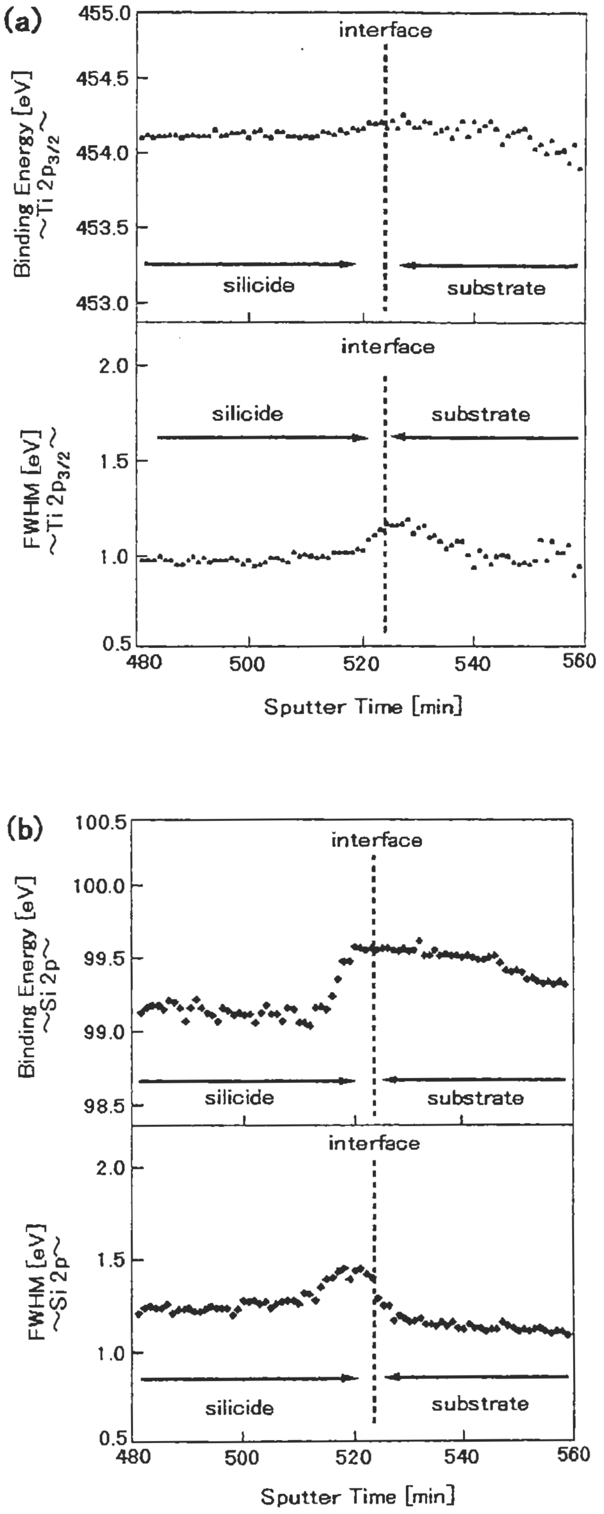

Fig.2 The XPS binding energy and full width at half maximum (FWHM) of (a) metal and (b) silicon peaks at silicide/silicon interfaces of $TiSi_2$ film for 0.5keV ion sputtering.

interfaces, respectively. In the case of TiSi$_2$, the binding energy of metal peak was almost constant and that of silicon peak increased. Although not represented in the figure, the binding energy of NiSi$_2$ had tendency similar to that of CoSi$_2$, and the binding energy of metal and silicon for WSi peaks decreased and increased, respectively. The FWHM of metal peak for all samples broaden at only interface. On the other hand, the FWHM of silicon peak for all samples except for TiSi$_2$ were almost constant at interface. In TiSi$_2$, the FWHM of silicon peak became broad at only interface. From the results of XPS binding energy and FWHM, I thought that two or more states of metal coexisted at only interface for all samples, and oxidized silicon existed at only interface for TiSi$_2$. It was reported that the native oxide existed at silicide/silicon interface [15-17]. Because XPS binding energy was not calibrated, we don't know whether XPS binding energy at interfaces changed due to original binding energy or electrification such as native oxide. Assuming that the peak shift uniformly occurred, we took the differences Δ (= BE_M - BE_{Si}) between XPS binding energy of metal (BE_M) and silicon (BE_{Si}) peaks.

Fig.3 shows the XPS binding energy differences Δ at silicide/silicon interfaces of (a) CoSi$_2$, (b) NiSi$_2$, (c) TiSi$_2$ and (d) WSi films for 0.5keV ion sputtering as a function of atomic concentration ratio. In Fig.3, the XPS binding energy differences Δ for CoSi$_2$ and NiSi$_2$ increased at silicide/silicon interfaces, whereas Δ for TiSi$_2$ and WSi decreased. In order to investigate the change of Δ before and after interfaces, we took the differences Δ_{after} - Δ_{before} between before and after interface. Here, Δ_{before} and Δ_{after} denote Δ at silicide region and interface in Fig.3, respectively.

Fig.4 shows the correlation of work function to Δ_{after} - Δ_{before} for ion sputtering of various energy. Freeouf et al. reported that Schottky barrier height, which was occurred by contacts between metal and silicide, had linear correlation to work function [9]. In Fig.4, there was a good linear correlation of work function to Δ_{after} - Δ_{before}. Therefore, Δ_{after} - Δ_{before} is linear correlation to work function of metal. We thought that Δ_{after} - Δ_{before} had relevance to Schottky barrier height at silicide/silicon interfaces.

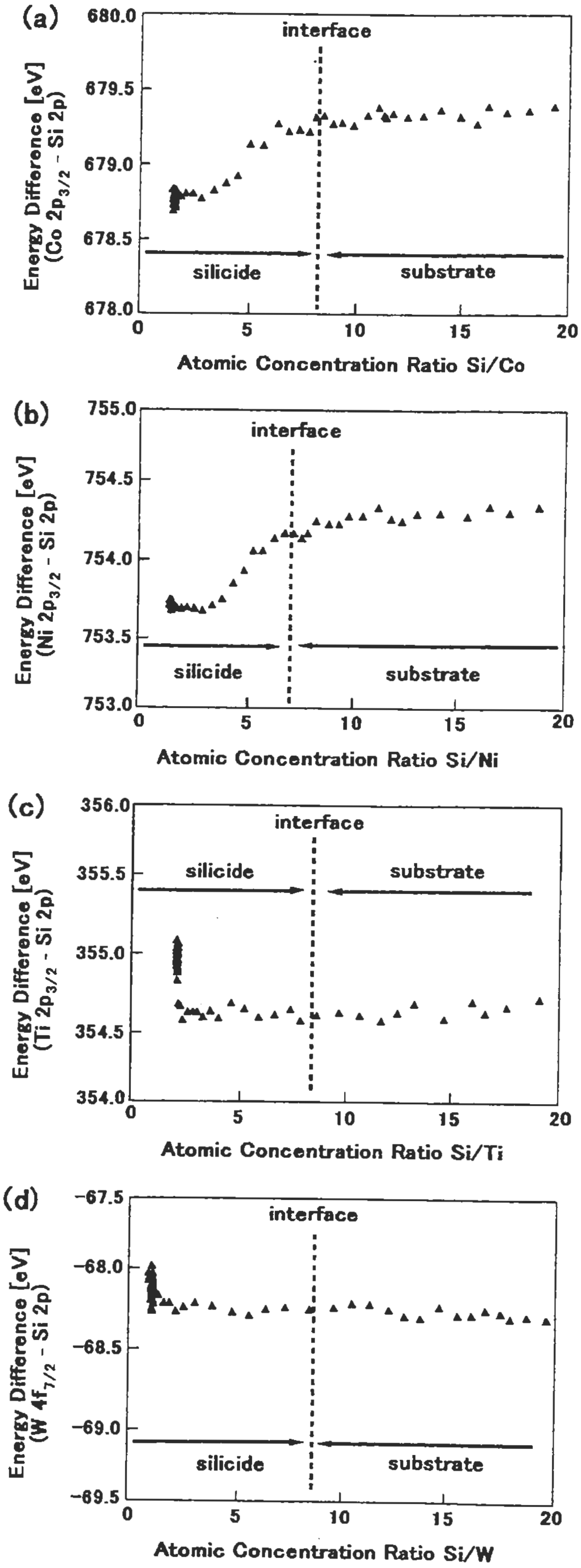

Fig.3 Δ at silicide/silicon interfaces of (a) CoSi$_2$, (b) NiSi$_2$, (c) TiSi$_2$ and (d) WSi films for 0.5keV ion sputtering as a function of relative atomic concentration ratio; Δ stands for the differences between XPS binding energy in metal and silicon peaks.

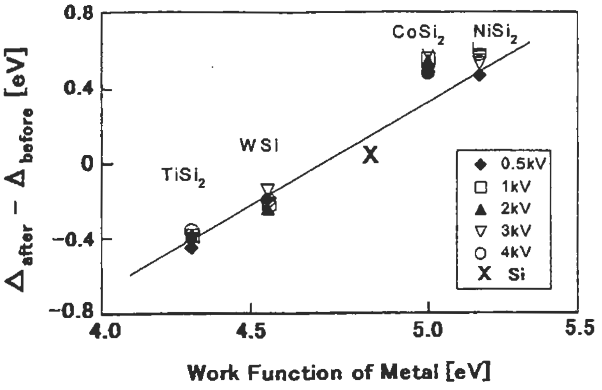

Fig.4 The correlation of work function to Δ_{after}- Δ_{before} for ion sputtering of various energy. Δ_{before} and Δ_{after} stand for Δ at silicide region and interface in Fig.3, respectively.

4.Conclusion

We measured binding energy change of them around silicide/silicon interfaces using X-ray photoelectron spectroscopy. From the results, we found that the XPS binding energy differences between metal and silicon peaks before and after silicide/silicon interfaces had a good correlation to work function and had relevance to Schottky barrier height at silicide/silicon interfaces.

5.References

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