The Possibility of Chemical State Analysis for Silicide Using XPS

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We are currently studying the application of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) in the characterization of materials used in the micro electronics industry. We have selected four transition metal silicides ($CoSi_x$, $NiSi_x$, $TiSi_x$, WSi_x) and examined whether it would be possible to perform a chemical state analysis to determine differences in their metallic properties using XPS.

The result of our experiments show that Auger parameter with respect to Si-$KL_{23}L_{23}$ spectrum excited by Bremsstrahlung X-rays are useful to study the chemical state of silicides instead of using only core level photoelectron spectra. We actually show that the use of XPS offers additional possibilities for chemical state analysis by using the negative binding energy region. Moreover, it is shown that AES equipped with concentric hemispherical analyser (CHA) offers nearly the same possibility except for the electron beam induced damage and the charge up problem that are related to that method.

1. INTRODUCTION

The objective of the Surface Analysis Society of Japan (SASJ) - Electronic materials Group (EMG) is to analyze problems in the characterization of semiconductor materials by AES and XPS and to share the related knowledge with each other.

Transition metal silicides have become one of the most important group of materials used in advanced microelectronics, due to their well-known properties [1]. These advantages include low wiring resistivity, low contact resistivity, thermal stability, and compatibility their in silicone-based large scale integrated (VLSI) device technology. Because of these advantages, silicides are used in gates as well as for interconnection and contact metallization in VLSI devices. In particular, self-align silicide (SALICIDE) technology is indispensable of new generation devices.

In this we have examined the possibility of using XPS for a chemical state analysis of four silicides.

2. EXPERIMENTAL SETUP

The silicides deposited on n-type Si(100) wafers up to a thickness of 200nm using co-sputtering were supplied by SASJ. Prior to the XPS analysis, all samples were examined by other analysis techniques in order to get information about their composition and crystal structure (see table 1). We used a non-doped silicon wafer (100) [1000 Ω·cm] which was made by floating zone (Fz) method to obtain a reference silicon spectrum.

All samples were chemically pre-cleaned in a diluted HF (HF:H_2O=1:50) solution for about

Table 1 Analytical results obtained by other technique.

	Composition ratio				Thickness	Impurity			Crystal structure	
Technique	ICP-AES	RBS			RBS	SIMS			XRD	
Silicide	Si/M	Si/M	Si/H	Ar/Si	(nm)	H	C	O	Structure	Grain size
CoSi$_x$	1.72	1.85	0.01	0.00	199	3.0E+18	5.0E+18	2.0E+18	amorphous	-
NiSi$_x$	1.89	2.02	-	0.00	193	3.0E+18	5.0E+18	2.0E+18	NiSi$_2$	42.8nm
TiSi$_x$	1.75	1.87	0.02	0.00	189	5.0E+18	3.0E+18	3.0E+18	amorphous	-
WSi$_x$	1.05	1.22	-	0.02	200	2.0E+18	3.0E+18	1.0E+18	amorphous	-

2 seconds and rinsed in ultra pure water for about 10 minutes to eliminate the native oxide. The surfaces of silicide and silicon usually tend to become covered by native silicon dioxide in air except $TiSi_x$. In the meantime $TiSi_x$ surface usually tend to covered by mixture oxide of titanium and silicon. After that, all samples were physically cleaned by Ar ion(2kV) in the XPS chamber. After physical cleaning was complete, only a small peak of O1s and C1s was observed in the XPS survey spectra (see figure 1).

The XPS measurements were performed with a Physical Electronics Inc. model-5400MC system. The experimental details are described in table 2. To ensure good electrical contact, all samples were screwed to the surface of the indium foil.

3. EXPERIMENTAL RESULT

The peaks that can be observed in the negative binding energy region of figure 1 are Auger electrons excited by the Bremsstrahlung which resulted from the Mg-Kα radiation. The spectrometer dose not measure the binding energy but rather the kinetic energy of the electrons. The binding energy can be obtained by correcting with following value ; the kinetic energy of photoelectrons, photon energy($h\nu$) and the work function (ϕ_s) of the spectrometer. Many young operators do not account for the existence and the value of Auger electrons that are excited by Bremsstrahlung X-rays and can be observed in the negative binding energy region.

Table 2 Experimental conditions of XPS measurement.

Instrument	Physical Electronics 5400MC			
X-ray source	Mg-Kα	400W(15kW,26.7mA)		
Take off Angle	45°			
Work function	4.55V			
Base pressure	2E-9Torr			
Acquisition details				
Survey	Pass Energy	143.05eV		
	Step	1eV/step		
High Resolution	Pass Energy	17.9eV[0.867eV(Ag3d5/2)]		
	Step	0.05eV/step		
Peak Energy	Cu2p3/2	Cu-LMM	Au4f7/2	Cu3p
This work	932.59	334.95	84.00	75.12
Seah's value	932.66	334.94	84.00	75.13

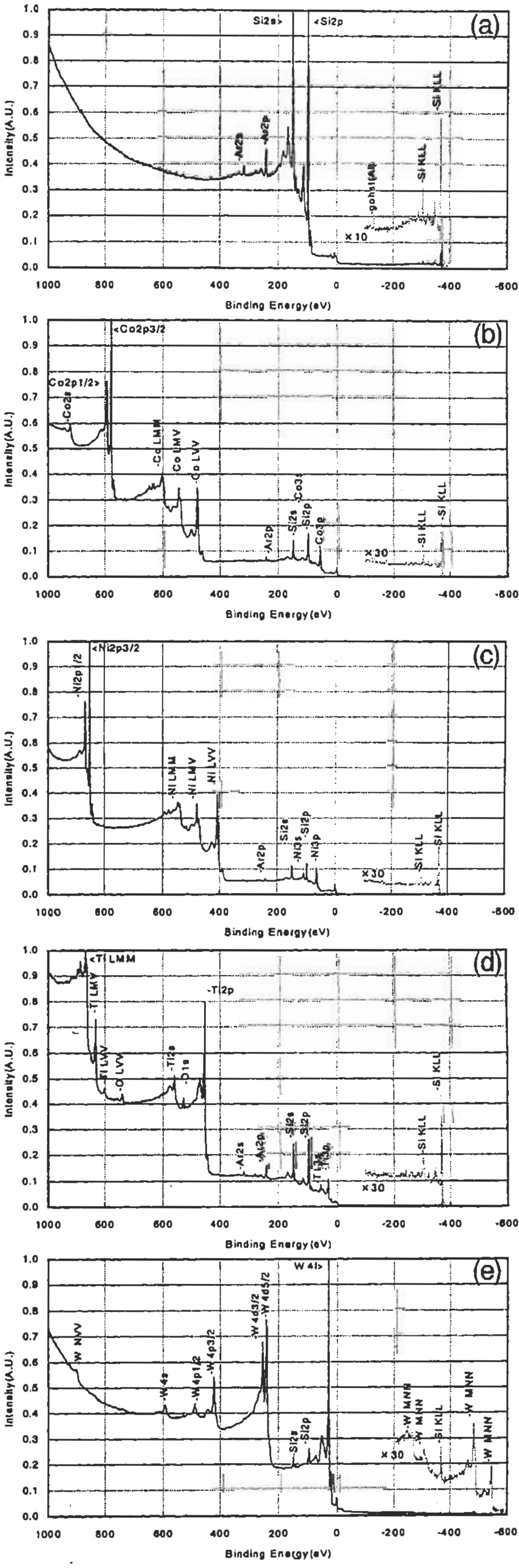


Fig. 1 Survey spectra of. (a)Fz Si, (b) CoSix, (c) NiSix, (d) TiSix and (e)WSix.

3-1 Peak position.

Figure 2 shows the Si2p, Si2s and Si-KL$_{23}$L$_{23}$ respective spectra in comparison to each other. The measurement of the peak position is the most simple and practical method for estimating the chemical state except there is charge effect. Table 3 lists binding energy of the Si2p, Si2s and Si-KL$_{23}$L$_{23}$ spectra from each silicide as well as the corrected peak position that was obtained using the peak position of the Ar2p spectrum (in parentheses). The table also includes the value of full width at half maximum (FWHM). The Ar signal comes from the Ar ion cleaning process. With regard to WSi$_x$, it was not possible to make such correction because it was not possible to detect the Ar2p peak, since it overlaps with the W4d5/2 peak. The differences in the peak energy between the photoelectron and the Auger electron (the so-called Auger parameters) are displayed in figure 3 as the function of the difference in the peak energy between the Si2p and Si2s. We used this parameter as we thought that charge referencing was not reliable enough. The Auger parameter (α) is a convenient parameter to analyze differences between the silicides while eliminating the charging effects. There is similar paper which investigated some kind of silicides with Auger parameter [3]. Further some paper have already addressed the effectiveness of Auger peaks for chemical state analysis compared to photoelectron peaks [4][5][6].

In general, there is a close correlation between the value of the photoelectron peak shift and electronegativity or electron-affinity. We have summarized these

Table 3 Peak position and full width of half maximum(FWHM).

		Si2s	Si2p	Si-KLL
FZSi	Peak position	150.72	99.43	-367.11
	(Corrected value)	(150.49)	(99.19)	(-367.35)
	FWHM	1.60	1.30	1.28
CoSi	Peak position	150.94	99.64	-367.63
	(Corrected value)	(151.30)	(100.00)	(-367.27)
	FWHM	1.89	1.55	1.38
NiSi	Peak position	151.03	99.70	-367.68
	(Corrected value)	(151.35)	(100.02)	(-367.36)
	FWHM	1.80	1.36	1.33
TiSi	Peak position	150.48	99.15	-368.01
	(Corrected value)	(150.09)	(98.76)	(-368.40)
	FWHM	1.76	1.35	1.28
WSi	Peak position	150.66	99.34	-367.59
	(Corrected value)	-	-	-
	FWHM	1.98	1.54	1.38

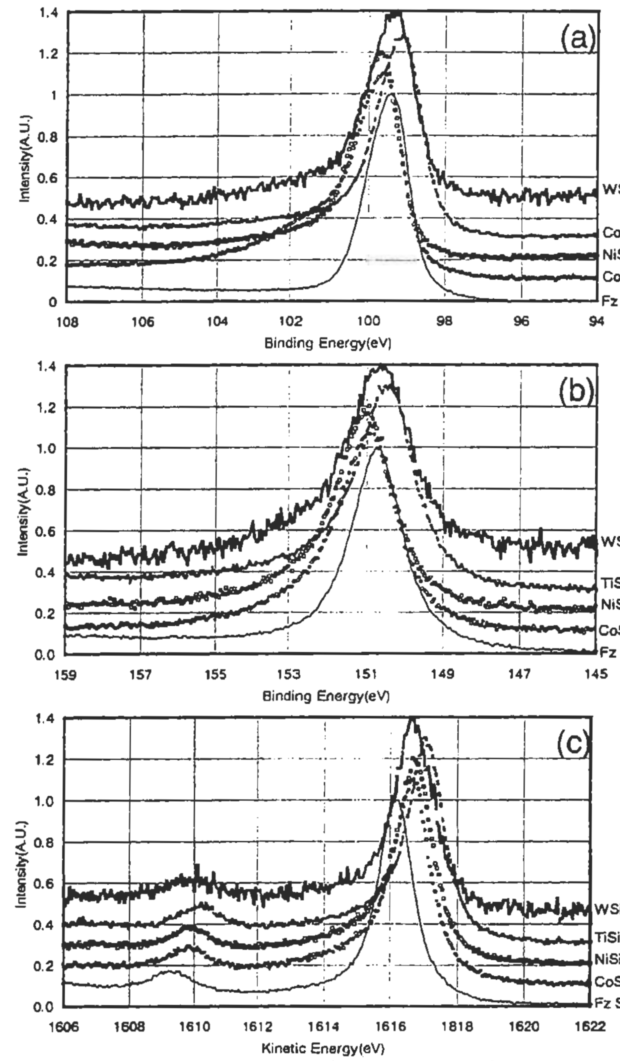


Fig. 2 High resolution spectra from each silicide. (a) Si2p, (b) Si2s and (c) Si KLL

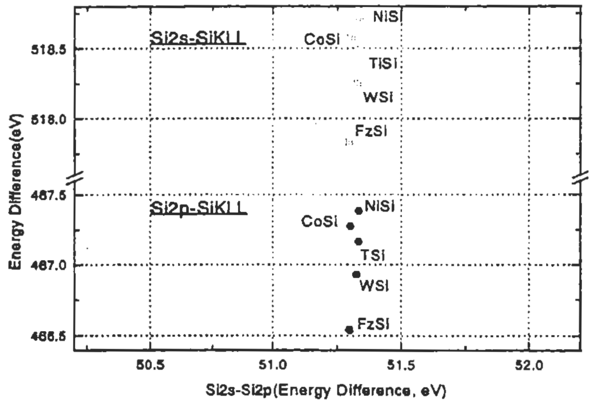
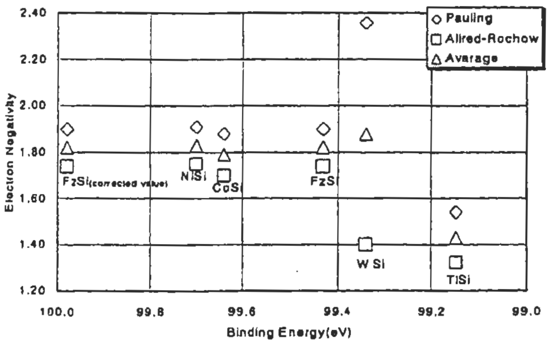


Fig.3 Energy differences between the peaks.

(a) Electronegativity



(b) Electron Affinity

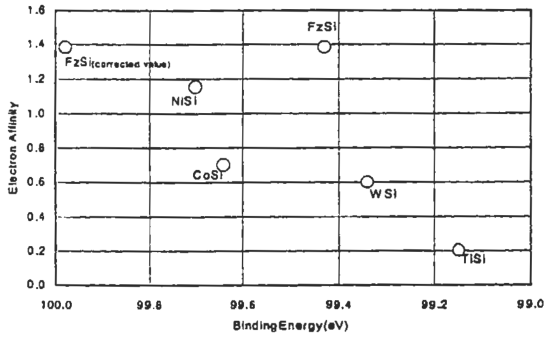


Fig. 4 The correlation of Si2p peak position to (a) electron negativity and (b) electron affinity.

relationships in figure 4. In photoelectron spectroscopy, photoelectron energy is usually referred to the Fermi level. We defined a corrected peak position which is obtained by adding 0.55eV (half the band gap of silicon) to the Si2p peak position of non-doped Fz-silicon to fit the Fermi level. Because the Fermi level of non doped Fz-silicon is located at the center of the band gap and the Fermi level of silicide is located in the conduction band. Figure 4 shows that there is a good correlation between the peak shift value of the photoelectron and electron affinity if charge referencing in our experiment is performed properly. On the other hand, electronegativity shows not such a good correlation to the peak shift value. The correction of peak position is not necessary if the peak position is defined from vacuum level.

3-2 Peak shape

In figure 2, it is easy to see that the shape of the silicon peaks for the silicides are similar regardless of the kind of silicide. All of the silicon peaks for the silicides show a tail in the high binding energy region which is not present to the peak of Fz Si. In the case of $CoSi_x$, the Si2p spectrum has a bigger tail as the Co3s peak overlaps with the Si2p peak. It is difficult to distinguish metallic species of silicides from the peak shape alone.

4. SUMMARY

We have examined a possible application of XPS for a chemical state analysis of silicides. We found that it is possible to identify the kind of the metal from the peak position of core level photoelectrons (Si2p and Si2s) if charge referencing is possible. There is a close relationship between binding energy and electron affinity. We conclude that Auger parameter using Si-$KL_{23}L_{23}$ spectra are useful to characterize the difference of silicides while eliminating charge effects. Many XPS users might not recognize the worth of Auger electrons that are exited by Bremsstrahlung X-rays, as their peak position is located in the negative binding energy region. By using the Auger parameter, the metallic differences of the silicides can be easily distinguished.

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