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Schottky-barrier heights of transition-metal-silicide–silicon contacts studied by x-ray photoelectron spectroscopy measurements

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Core-level energy shifts and chemical shifts of transition metals on silicide formations are measured by use of x-ray photoelectron spectroscopy for 10 different silicides. The linear correlation is found between the chemical shifts and silicide–*n*-type Si Schottky-barrier heights. This correlation shows that Schottky-barrier heights are proportional to the energy shifts of valence *d* bands of transition metals on silicide formations. Roles of chemical bonds in Schottky-barrier heights are discussed.

I. INTRODUCTION

Recently, transition-metal (TM)–silicide/Si contacts have been extensively studied due to their technological importance and scientific interest. Above all, the mechanism of the Schottky-barrier formation for these contacts has been investigated and its parameters have been proposed by many authors.[1–6] In 1975, Andrews and Phillips[1] correlated Schottky-barrier heights (ϕ_b) to the heat of formation of the silicide (ΔH_f), which represented the bonding nature of silicides.[1] They successfully showed a simple linear relation (except for PtSi) between ϕ_b and ΔH_f. In 1986, Bucher *et al.*[6] showed that the lower-barrier TM-silicide–*n*-type Si values appeared to correlate linearly with the original correlation parameter, the work function of TM silicide (ϕ_{silicide}), and the correlation was comparable to the case for metallic elements, although it did not seem to make sense to correlate ϕ_b and ϕ_{silicide} for noble-metal silicides (Os, Ir, and Pt silicides).[6] On the other hand, Tove[4] and Schmid[5] found that elemental parameters, such as work function (ϕ) and electronegativities of metal and Si, correlated better than the relevant electronic parameters of silicides. Tove showed that the work function of metal (ϕ_m) gave a result which was at least not inferior to other approaches, if one included recent data for rare near-noble metals and rare earths and plotted the results for periods 6, 5, and 4 of the transition elements, respectively.[4] Tove explained the correlation as being due to "induced dipole" at the interface, whose magnitude depended on the work function of the metal. Schmid showed that there was a definite correlation between Miedema's electronegativity for the transition metal and ϕ_b.[5] He explained the correlation by an "interface bond model," where the interface Fermi level was pinned in the bonding states and the bonding states' energy values were correlated with Miedema's electronegativity.

Thus, conventional parameters for silicides, such as ϕ_{silicide} and ΔH_f, are somehow inappropriate, while some elemental parameters, including the work function and electronegativity for metals are related more directly to ϕ_b. In this paper, the authors again correlate ϕ_b with parameters for silicides (bonding natures for silicides) directly by x-ray photoelectron spectroscopy (XPS). Core-level energy shifts (chemical shifts) for transition metals on silicide formation were measured by the XPS method and were found to be proportional to Schottky-barrier height without exception. This correlation is discussed from the standpoint of the bonding nature of silicides and seems to support some Schottky-barrier models.

II. EXPERIMENT

(100) crystalline Si wafers were used as substrates for thin-TM-film deposition. Prior to the deposition, the substrates were cleaned using standard chemical procedures and annealed at above 800° C in an ultrahigh-vacuum chamber, whose base pressure was less than 5×10^{-8} Torr. The TM's, $_{22}$Ti, $_{27}$Co, $_{28}$Ni, $_{42}$Mo, $_{46}$Pd, $_{73}$Ta, $_{74}$W, and $_{78}$Pt were evaporated by a conventional electron-beam gun. Half the group of the deposited samples were annealed in a flowing N_2 atmosphere or in an ultrahigh-vacuum chamber at an appropriate temperature.[7] The other half remained in as-deposited conditions. The silicide formations were identified by x-ray diffraction. Only one silicide phase was confirmed in each sample by the observation of single-peak shapes of the TM core levels, independent from the depth at which XPS spectra were obtained. Prior to XPS measurements, surfaces of the samples were scraped by a knife made of B_4C. No oxygen or carbon was detected on them. The XPS measurements were performed using a Hewlett-Packard HP5950A spectrometer (0.1 eV resolution) with a monochromatized x-ray source (Al $K\alpha$ $h\nu=1486.6$ eV). Sample surfaces were electrically shorted to the analyzer. Core-level energy (E_b) and chemical shift (ΔE_b) were measured for the TM core levels. ΔE_b was assigned as positive, when E_b for the level in a silicide was larger than that in a TM.

Measured ΔE_b values are shown in Table I. ϕ_b values for various silicide–n-type Si contacts are also listed in Table I, from Refs. 1 and 6. A correlation between ϕ_b and the ΔE_b is shown in Fig. 1. A trend toward increasing ϕ_b with increasing ΔE_b is shown by the solid line. The solid line is the result of a least-squares fit to the data,

$$\phi_b = K\,\Delta E_b + C\ , \tag{1}$$

where $K=0.11$ and $C=0.62$.

The data point for PdSi was assumed on the solid line, according to its ΔE_b, because no ϕ_b data for PdSi was available. The very outstanding feature is the linearity between ΔE_b and ϕ_b, without any exception, over nine different silicides. Note that PtSi, which was the exception in the previous model,[1] is no longer an exception.

III. DISCUSSION

Since core-level energy E_b values were measured with respect to Fermi energy of the analyzer, it makes no sense from the energy standpoint to compare ΔE_b for different silicides. Therefore, core-level energy (E_c) and its shift (ΔE_c) with respect to the vacuum level was used to discuss them in connection with ϕ_b, which is determined with respect to Si bulk energy. E_c is given by

$$E_c = E_b + \phi_s\ , \tag{2}$$

where ϕ_s is a work function for a sample. ΔE_c is given in terms of ΔE_b and $\Delta\phi_s$ by

$$\Delta E_c = \Delta E_b + \Delta\phi_s\ , \tag{3}$$

where $\Delta\phi_s$ is the difference between work functions for Tm and silicide.

Substituting the value of ΔE_b from Eq. (3) in Eq. (1) we obtain

$$\phi_b = K\,\Delta E_c - K\,\Delta\phi_s + C\ , \tag{4}$$

where $\Delta\phi_s$ can be obtained for 10 different silicides by using available data for ϕ_{metal} (Ref. 8) and ϕ_{silicide}.[6]

Using the above data in Eq. (4), ϕ_b was found to be proportional to ΔE_c as well as ΔE_b, as shown in Fig. 2. Barrier height was found to increase from 0.63 eV with increasing positive chemical shift and decrease with increasing negative chemical shift. The correlation is represented by Eq. (5):

$$\phi_b = 0.15\,\Delta E_c + 0.63\ . \tag{5}$$

This solid line is well fitted even for the Pt silicides of different compositions. ϕ_b increases with increasing ΔE_c, as Pt content in platinum silicide decreases. This ϕ_b increase is quite a contrast to the prediction of the Schottky model,[9] because $\phi_{\text{platinum silicide}}$ seems to decrease with decreasing Pt content,[6] becoming more Si-like. Therefore, the mechanism for determining ϕ_b is not explained by the Schottky model, but by a model taking into account the

TABLE I. Measured transition-metal core levels and the core-level energy shifts with respect to Fermi level (ΔE_b) on silicide formation, and barrier heights for silicide–n-type Si contacts (ϕ_b). Core-level energy shifts were assigned as positive when the binding energies for the levels in silicides were larger than those in metals. Barrier heights were taken from Refs. 1 and 6.

Silicide	Measured metal core level	ΔE_b (eV)	ϕ_b (eV)
PtSi	$4f\,\frac{7}{2}$	1.9	0.88
Pt_2Si	$4f\,\frac{7}{2}$	1.5	0.85
PdSi	$3d\,\frac{5}{2}$	2.0	
Pd_2Si	$3d\,\frac{5}{2}$	1.4	0.75
NiSi	$2p\,\frac{3}{2}$	1.0	0.66
$CoSi_2$	$2p\,\frac{3}{2}$	0.4	0.65
$TaSi_2$	$4f\,\frac{7}{2}$	0.4	0.59
WSi_2	$4f\,\frac{7}{2}$	0.0	0.65
$TiSi_2$	$2p\,\frac{3}{2}$	−0.2	0.60
$MoSi_2$	$3d\,\frac{5}{2}$	−0.3	0.65

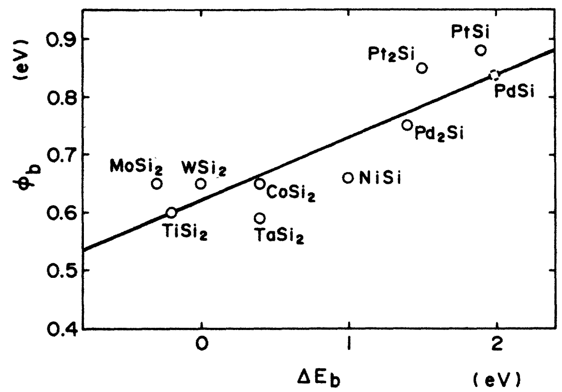

FIG. 1. Barrier heights for silicide–n-type Si contacts (ϕ_b) vs transition-metal core-level shifts with respect to Fermi level (ΔE_b) on silicide formation. The data point for PdSi was assumed on the solid line, according to its ΔE_b, because no ϕ_b data for PdSi were available. $\phi_b = 0.11\,\Delta E_b + 0.62$.

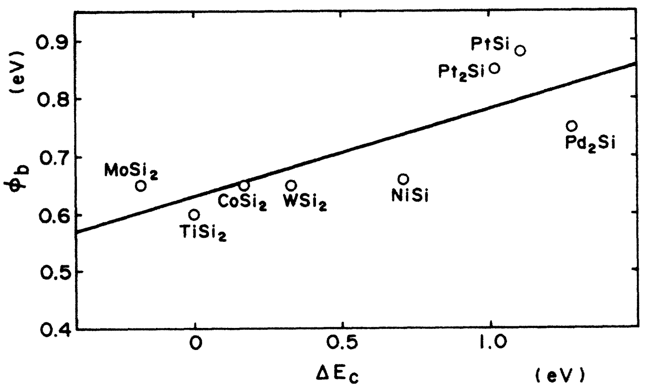

FIG. 2. Barrier heights for silicide–n-type Si contacts (ϕ_b) vs transition-metal core-level shifts with respect to the vacuum level (ΔE_c) on silicide formation. $\Phi_b = 0.15\,\Delta E_c + 0.63$.

chemical bonding which is reflected in core-level energy shifts.

We started to consider ΔE_c [the first term in the right-hand side in Eq. (5)] to obtain information regarding the chemical bond nature of silicides which is related to ϕ_b. E_c for TM is known to increase in energy according to the positive energy shift at the center of the valence d band of TM (ΔE_d), due to the decrease in the number of valence d electrons or in the screening effect.[10,11] In silicide, such a d band is the bonding band to first approximation between TMd orbitals (TMd–TMd bonding band) with higher density of states,[12] but not the bonding or the antibonding band between Si p orbitals and TM d orbitals (Sip–TMd bonding or antibonding band) which have a lower density of states.[12]

In fact, the linear correlation between ΔE_c and ΔE_d for silicides can be seen in Fig. 3. Here ΔE_d values are obtained from the energy shifts with respect to the vacuum level of the main peaks in the valence band spectrum[13–19] of silicides compared with those for metal. Since the photoionization cross section of the TMd–TMd bonding band is dominant compared with that for the Si band and the Sip–TMd bonding band,[17] the spectral feature can be associated directly with structures in the density of states,[20] especially with d bands, for photon energy larger than 24 eV.

From Fig. 3 it is found that ΔE_c increases with increasing ΔE_d. This is caused by a decrease in the number of electrons in the TMd–TMd bonding band. It is considered that this reduction in electrons of a TMd–TMd bonding band is caused by substituting Sip–TMd bonds, which is more directional in character, for some parts of TMd–TMd metallic bonds: charge transfers from TMd–TMd bonding bands to TMd–Sip bonding bands. This is confirmed by the fact that the energy difference between the TMd–TMd bonding band and the *TM d*–Sip bonding band decreases as ΔE_c increases.[16] The increase in the relative intensity of the Sip–TMd bonding band compared to the TMd–TMd bonding band[16] is also consistent with the above discussion.

Together with the result shown in Fig. 2, it is concluded that ϕ_b increases as electrons decrease in TMd–TMd bonding bands in silicides. Thus, the nature of TM bonds in silicides (ΔE_d or ΔE_c) is found to be a more appropriate description for ϕ_b compared with conventional parameters for silicides, such as ΔH_f and ϕ_{silicide}. The reason is as yet unclear, but it seems that ΔE_d is correlated with the change in the interface Fermi level, which includes either an internal Fermi level[21] or an interface bonding state level.[5] At first, Schluter proposed an internal work function (internal Fermi level) for an appropriate work function, without an additional electrostatic contribution from a metal surface dipole.[21] Recently, Schmid's report assumed that an interface Fermi level was pinned in interface bonding states with high density at the silicide–Si interface and that the change in ϕ_b is not determined by the change in ϕ_{silicide} (bulk Fermi energy), but that it is determined by the change in interface bonding states energy (interface Fermi energy).[5] Such models seem to be supported by this work because the nature of the bonding is found to be the same both for the bulk and the interface.[19]

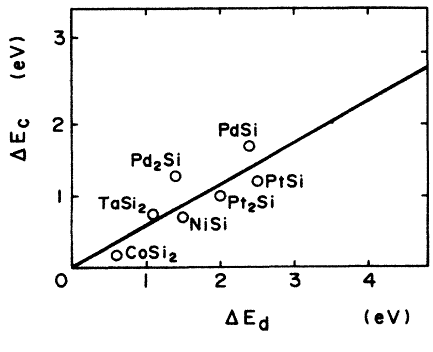

FIG. 3. Transition-metal core-level energy shifts with respect to the vacuum level (ΔE_c) vs energy shifts of bonding band between d orbitals of transition metal (ΔE_d), on silicide formation.

On the other hand, it may also seem that ΔE_c is correlated with an interface dipole,[22] because charge shift in spatial region would produce a dipole. The microscopic interface dipole magnitude is within about 0.3 eV, simply predicted by the charge transfer which is estimated from the difference in Pauling electronegativity. It can account for the deviation in ϕ_b from the Schottky model. In fact, P. J. Grunthaner *et al.* found that ϕ_b correlated with the strength of the TM-Si orbital interaction as well as the charge density around the Si atoms for Ni, Pd, and Pt silicides by XPS measurements.[19] They supposed that the charge density around the Si atoms at the single-crystal Si interface which had at least one TM-Si bond played the dominant role in determining the ϕ_b. Since the apparent charge density increased in the order Ni-Si < Pd-Si < Pt-Si, they therefore expected a corresponding scale in interfacial dipole strength and attendant increase in Si band bending. However, precise knowledge about the microscopic structures and the charge distributions at the interfaces are required to discuss further the correlation between ϕ_b and the interface dipole.

Finally, we will briefly mention the interface structure induced effects which were neglected in the above discussion. Although, there is uncertainty as to the interface structure of silicides in this experiment, as well as in the barrier height data,[1,6] the interface effects caused by the change in interface structure is found to be of the second order for determining ϕ_b, as follows. Recently, ϕ_b of $NiSi_2$–Si(111) was found to depend on the interface structure and the origin was discussed by some groups. Tung found a substantial difference of 0.14 eV between ϕ_b values for type-A and type-B $NiSi_2$–n type Si (111), though the structures for these two interfaces are very similar, differing only in the positions of the third and higher-nearest neighbor to the last nickel layer.[23] On the other hand, Liehr *et al.* found a 0.12 eV reduction in ϕ_b on the interface perfection degradation for $NiSi_2$–n-type Si(111) structure.[24] They found type-A and type-B $NiSi_2$ with near-perfect interfaces had the same barrier height of 0.78 eV and that those with imperfect interfaces had a lower-barrier height of 0.66 eV. They also showed that this change was related to the change in interface states.[25] These observations suggest that interface effects, due to either the interface atomic coordination or interface states, are only 0.12–0.14 eV, which is within the error limits in the present measurements. Therefore the observed chemical trend for ϕ_b is caused by the change in chemical bond nature in silicides, as discussed above. This trend will be improved when more precise data of ϕ_{silicide}, ϕ_b and ΔE_d values are obtained.

CONCLUSIONS

The authors measured chemical shifts in metal core levels on silicide formations by the use of XPS. Linear correlation was found between the chemical shifts in metal core levels and silicide–n-type Si Schottky-barrier heights. This correlation shows that Schottky–barrier heights are proportional to the energy shifts of TM d–TM d bonding bands, which are caused by the changes in the number of TM d–TM d bonding electrons on silicide formations. This correlation seems to support the Schottky-barrier models which propose an interface Fermi level differing from the bulk Fermi level.

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