Appl. Phys. A 40, 71–77 (1986)

Applied Physics A Solids and Surfaces



# Work Function and Barrier Heights of Transition Metal Silicides

E. Bucher, S. Schulz, M. Ch. Lux-Steiner, and P. Munz
Universität, Fakultät für Physik, D-7750 Konstanz, Fed. Rep. Germany

U. Gubler
Physikalisches Institut, Universität, CH-4000 Basel, Switzerland

F. Greuter*
Laboratorium für Festkörperphysik, ETHZ, CH-8093 Zürich, Switzerland

Received 15 January 1986/Accepted 10 March 1986

**Abstract.** The work function of 13 polycrystalline transition metal silicides was measured by photoemission in uhv. Their values are discussed in relationship to their Schottky barrier heights on n-Si. While there appears to be a weak correlation for a certain group of transition metal silicides, the values of the 5*d*-noble metal silicides including some of the lattice matched Ni silicides appear to be completely uncorrelated. Experimental values of work functions are compared to the values proposed previously by Freeouf.

**PACS:** 73.40

One of the basic problems in device research is the prediction of device parameters from the electronic properties of their components.

For barrier heights $\phi_B$ between n-silicon and transition metal silicides the question arises whether $\phi_B$ is correlated to parameters related to silicon and metallic elements or silicon and transition metal silicides (tm-Si) [1–5]. In 1975, Andrews and Phillips [6] found a linear correlation between $\phi_B$ and $\Delta H_f$, the heat of formation of the barrier forming tm-Si. However, as more data became available [7–9] and some values of $\Delta H_f$ were revised [10], the $\phi_B - \Delta H_f$ correlation lost some ground. Another interesting correlation between $\phi_B$ and eutectic temperatures in tm-Si systems was found by Ottaviani et al. [11, 12], representing also a correlation between properties of silicon and silicides. In the Ottaviani plot many anomalies in the Andrews-Phillips plot [6] are removed, in particular those arising from 5*d*-noble metal silicides. The theoretical background, however, for this fact still remains obscure because the eutectic temperature depends on many thermodynamic variables in a complex way (such as chemical activities, heat and temperatures of fusion of individual components as well as excess free enthalpies of both components [13]). In contrast, Schmid [1] has very recently plotted $\phi_B$ values vs. Miedema's revised electronegativities of metals [14], thereby correlating the barrier heights to elemental individual parameters. Some deviations from a linear relationship in Schmid's plot are still present [1]. It is indeed difficult to imagine that one simple parameter may account for the barrier height depending on many complex parameters such as interface density of states [15], doping etc. [16]. As an example, it was shown for the n-Si [11]/$NiSi_2$ and NiSi interface that $\phi_B = 0.65$ eV could be raised to 0.78–0.79 eV for the defect free interface [17, 18], the higher $\phi_B$ corresponds to the value expected from a linear $\phi_B$ vs. electronegativity (Miedema's values) [1] relationship. It is expected that $NiSi_2$ is representative for other tm-Si systems although $CoSi_2$ failed to exhibit such a $\phi_B$ enhancement [19]. It has been

* Now at BBC, Baden, Switzerland

Table 1. Heats of formation $\Delta H_f$ for transition metal silicides (calculated per mole of transition metal atoms), their barrier values on n-Si, some of their work functions $W$, resistivities and residual resistivity ratios. Among the considerable scatter in $\phi_B$ values we have chosen the most likely values and those consistent with our device analysis

| Compound | $\Delta H_f$ [eV] [10] except others are given | $\phi_B$ [eV] Ref. | $W$ [eV] This work | $\varrho$(300 K) [μΩcm] This work except where Ref. given | $\frac{\varrho(300\,K)}{\varrho(4.2\,K)}$ This work | Remarks |
|---|---|---|---|---|---|---|
| $TiSi_2$ | 1.39 | 0.60 [7, p. 292] | 4.53±0.03 | 14 | 47 | |
| $VSi_2$ | 3.26 | 0.64 [37] | 4.63±0.03 | 50 [8] | | |
| $CrSi_2$ | 1.28 | 0.57 [7] | 4.32±0.02 | 600 [8] | | *p*-type semicond. |
| MnSi | 0.63 [14] | 0.65 [38] | | 220 [38] | | |
| $MnSi_{1.7}$ | | 0.67 [38] | | 4100 [38] | | |
| $FeSi_2$ | 0.84 | 0.68 [37] | | > 1000 [8] | | |
| CoSi | 0.96 [14] | 0.68 [7] | | 120 [8] | | |
| $CoSi_2$ | 1.07 | 0.64 [7] | 4.77±0.1 | 24 | 6.3 | |
| $Ni_2Si$ | 0.77 | 0.66 [39] | 4.96±0.01 | 22 | 19 | $\phi_B$=0.7–0.75 eV given by [7] |
| NiSi | 0.93 [14] | 0.65 [18] | | | | $\phi_B$=0.78 eV if lattice matched [18] |
| $NiSi_2$ | 0.91 | 0.66 [17, 18] | | 50 [8] | | $\phi_B$=0.79 eV if lattice matched [17] |
| $YSi_{1.7}$ | | 0.39 [40] | | | | $\phi_B$=0.75 eV on ⟨100⟩p-Si and 0.69 eV for Y metal |
| $ZrSi_2$ | 1.65 | 0.55 [7] | | 35 [8] | | |
| $NbSi_2$ | 1.43 | 0.63 [37] | | 50 [8] | | |
| $MoSi_2$ | 1.13 | 0.65 [37] | 4.82±0.05 | 100 [8] | | $\phi_B$=0.55 eV given by [7] |
| $Ru_2Si_3$ | | 0.72±0.02 [33] | | | | $\phi_B$=0.79 eV for Ru metal $Ru_2Si_3$ is semicond. |
| RhSi | 1.27 | 0.75 [41] | | 164 [41] | | $\phi_B$=0.81 eV for Rh metal [41] |
| $Pd_2Si$ | 1.25 | 0.71 [39] | 5.0±0.03 | 30 [8] | | $\phi_B$ dep. on heat treatment [39, 42]; $W$=5,40 eV [30] |
| HfSi | 1.48 [14] | 0.53 [7] | | | | |
| $HfSi_2$ | 2.35 | | | 45 [8] | | |
| $TaSi_2$ | 1.24 | 0.59 [7] | | 33 | 21 | |
| $WSi_2$ | 0.96 | 0.65 [7] | 4.88 | 70 [8] | | |
| $ReSi_2$ | 0.94 | 0.77 [37] | | 2300 | 1.6 | $\phi_B$ corresponds to Re metal; semicond. $\Delta E_g \sim 0.2$ eV |
| $OsSi_{1.8}$ | 1.07 [45] | 0.85 [37] | 4.75±0.07 | $9 \cdot 10^4$ | 0.4 | traces of 2nd phase |
| IrSi | 1.39 | 0.93 [8] | 5.08±0.03 | | | |
| $Ir_2Si_3$ | 0.80 [45] | 0.85 [8] | | | | |
| $IrSi_3$ | 0.79 [45] | 0.94 [8] | 4.68±0.1 | 810 | 1.2 | $p^+$ type semicond. |
| $Pt_2Si$ | 1.11 | 0.85 [42] | 5.17±0.01 | 6.5 | 66 | |
| PtSi | 1.75 | 0.88 [42] | 4.86±0.05 | 28 [8] | | $\phi_B$=0.21±0.05 eV for p-Si [45]; $W$=4.97± 0.02 eV [30] |
| SiAu | 0.09 [6] | 0.80 [7] | | | | |
| $GdSi_2$ | | 0.37 [40] | | | | $\phi_B$=0.71 eV for p-Si [40] |
| $DySi_2$ | | 0.37 [40] | | | | $\phi_B$=0.73 eV for p-Si [40] |
| $HoSi_2$ | | 0.37 [40] | | | | |
| $ErSi_2$ | | 0.39 [40] | | | | $\phi_B$=0.70 eV for p-Si [40] |
| $ErSi_{1.7}$ | | 0.40 [43] | | | | ⟨100⟩n-Si, $\phi_B$=0.77 eV for ⟨100⟩p-Si [43] |

suspected previously [15, 20] that high $\phi_B$ values are related to defect-free lattice matched systems. This is also indirectly confirmed by various solar cell studies in tm-Si/n-Si solar cells that open-circuit voltages $V_{oc}$ are highest for cells with improved interfaces and lowest interface density of states (since $V_{oc} \sim \phi_B$) [21–23].

Andrews and Phillips have speculated that anomalously high barriers (PtSi/Si) could be due to ionic electron charge transfer from Pt to interface states. Following the publication of the Andrews-Phillips plot, we tried alternatively to relate some of its anomalies arising from 5*d*-noble metal silicides to their possible anomalous work functions. We have extended previous studies [24] now to 13 systems including metallic and also semiconducting silicides (Table 1). The results of our studies will be presented and discussed.

## 1. Experimental Procedure

### *1.1. Sample Preparation*

The silicides whose work functions, *W*, are reported in column 4 of Table 1 were arc melted in an argon arc furnace under very pure conditions using 5*N* argon with oxysorb devices. The arc cast buttons were remelted several times. Many silicides under investigation are difficult to prepare, and had to be made over several times. They tend to shatter either during the fusion process or during remelting. The stoichiometry of the final melt could be substantially improved by presintering the silicides from mixed powder (60–100 μm) for 36–48 h at 1000°C. This led in most cases to single phase material.[1] The polycrystalline ingots consisting of crystallites of 50–300 μm size were all single phase except $OsSi_{1.8}$ which showed also traces of $OsSi_{1.5}$, the latter, however, is not identical to the orthorhombic $Os_2Si_3$ [25]. No attempt was made to analyze the traces of the 2nd phase. $OsSi_{1.8}$ could only be obtained single phase by powder metallurgical methods which, however, did not lead to acceptable samples for work function measurements. Controversy also exists regarding stoichiometry of $ReSi_2$. $ReSi_{1.8}$ invariably showed traces of ReSi. Our results on $ReSi_2$ are in close agreement with those of Siegrist et al. [26].

### *1.2. Work Function Measurements*

Work function measurements were performed in uhv at pressure below $10^{-10}$ mbar. From the melted buttons bars about 15 mm long and approximately 10 $mm^2$ crossections were cut. 3 samples were loaded on a sample holder highly isolated by glassy ceramics. Several grooves were cut at the end of the samples to set cleavage areas under uhv conditions. The samples were cleaved at pressures of $2 \times 10^{-9}$ mbar in an interlock chamber separated by an all-metal valve from the main chamber and moved immediately into the optical uhv chamber kept at pressures of $2 \times 10^{-11}$ mbar. Samples were kept at potentials between $-6$ to $-10$ V with respect to the vacuum chamber to avoid spurious photoelectric currents due to reflected light beams, arising from other sources than the cleaved sample. A sputtered polycrystalline Ir film was used as a test measurement leading to a work function of 5.24 eV in good agreement with the literature (5.27 eV) [27]. Photocurrents were measured at the sample with a Keithley Ammeter. The spectral range between 200 nm (=6.21 eV) and 300 nm (=4.14 eV) of a 150 W high pressure Xe lamp was used as a photon source. The photon energy was varied in steps of 0.1 eV and plotted vs. $j^{1/2}$ (or $j^{1/3}$ for semiconductors $CrSi_2$, $OsSi_{1.8}$). The linear extrapolation of $j^{1/2}(=Y^{1/2})$ and $j^{1/3}(\sim Y^{1/3})$ (where $Y$ is the yield) to $j=0$ was chosen as the relevant work function of the material (Fowler's method [28]). The work function in different crystallographic directions can vary appreciably. Our values with a light spot of 2 mm on samples with grain sizes of 50–300 μm, therefore, represent some average values of $W$ (averaged over crystallographic orientations). In order to avoid possible irrelevant values from specific orientations measurements were repeated 2–3 times on different freshly cleaved surfaces. Figure 1 represents typical results on 3 different silicides. The reproducibility can be considered as quite satisfactory. The uncertainty of the work function in most cases is $\pm 0.02$–$0.05$ eV. The $W$ values given in column 4 of Table 1 are averaged values of 2 or 3 measurements on different areas.[2]

### *1.3. Resistivity of Silicides*

Some of our silicides were further characterized by resistivity measurements between 4.2 and 300 K. Among our 13 silicides $CrSi_2$, $OsSi_{1.8}$, $ReSi_2$, and $IrSi_3$ are semiconductors (p-type degenerate in our case). The resistivity values were obtained by the standard 4-point method. Room temperature values and residual resistivity ratios [$RRR \equiv \varrho(300\,K)/\varrho(4.2\,K)$] are also reported in Table 1. For metallic silicides RRR values range between 10–100 which is typical for polycrystalline fine grained intermetallic compounds.

[1] The starting elements were better than 99.99% (99.9999% for Si). The quality of the silicides is evaluated from the residual resistivity, given in Table 1

[2] Exposure of freshly cleaved surfaces to a residual pressure of $10^{-10}$ mbar shifted $W$ by about 0.01–0.015 eV/h to higher values (measured for $Pd_2Si$, $MoSi_2$, PtSi, and $WSi_2$ only)

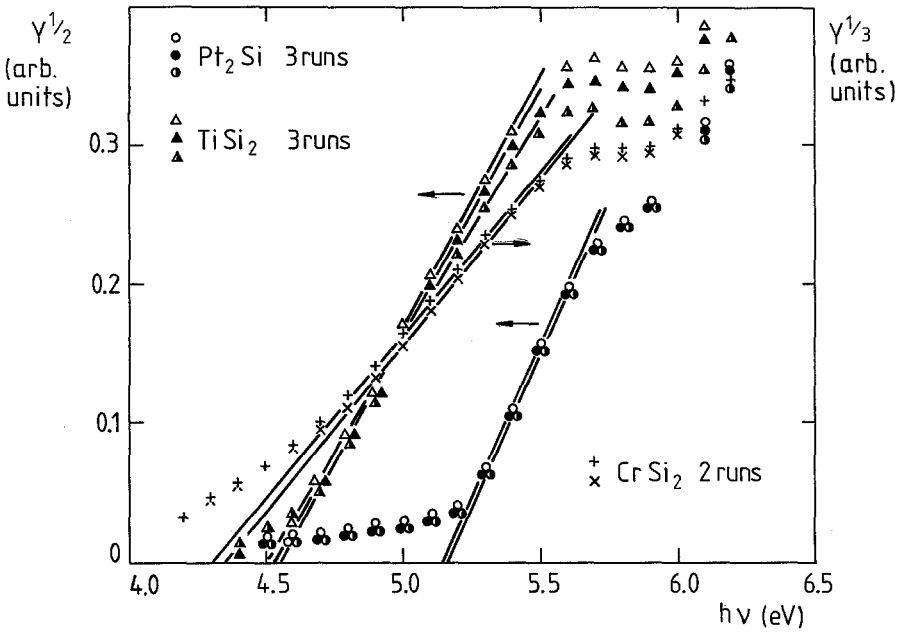


Fig. 1. Photoemission yield of 3 transition metal silicides $TiSi_2$, $Pt_2Si$, $CrSi_2$

### *1.4. Device Properties of Silicides*

Silicon/silicide systems have been intensely investigated in particular because of their potential applications [8]. Their fabrication as photovoltaic detectors, for example, is expected to be very simple. The extreme hardness and chemical stability [8] of silicides, in particular noble metal silicides, makes such devices potentially very attractive. We have tested photovoltaic devices recently made by reaction of thin (30–50 Å thick) metal films of Ti, Co, Ni, Os, Ir, Pt and found efficiencies between 1–4% only [21–23]. They are true majority carrier devices with low open-circuit voltages between 300–400 mV under AM 1.5. The best devices could be obtained with Pt and Ir as expected from their highest barrier values. The barrier values listed in Table 1 were also verified in our study by our photovoltaic devices. For solar energy conversion, however, these devices cannot compete with MIS and p/n junctions capable of achieving much higher open-circuit voltages and efficiencies.

## 2. Discussion

All silicides with known barrier heights and work functions are plotted in Fig. 2. Work functions of NiSi and $NiSi_2$ were guessed from $CoSi_2$ and from comparison with other noble metal silicides such as $Pt_2Si$, PtSi, $Pd_2Si$, $Ni_2Si$. The work function, e.g., of NiSi was evaluated as 4.68 eV from $W_{NiSi}/W_{Ni_2Si} = W_{PtSi}/W_{Pt_2Si}$. They are considered as highly plausible $W$ values but were not included in the numerical analysis. The high $\phi_B$ values of NiSi and $NiSi_2$ correspond to lattice

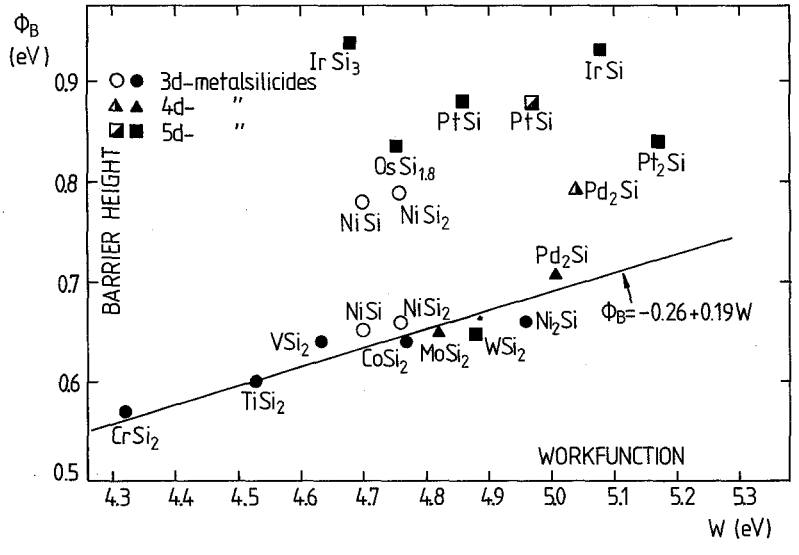


Fig. 2. Barriers $\phi_B$ of n-Si vs. work functions $W$ of silicides. The higher $\phi_B$ values of NiSi and $NiSi_2$ correspond to highly ordered interfaces [17, 18] the higher values work functions for $Pd_2Si$ and PtSi were taken from [30]. Filled symbols: exp. values, empty: evaluated values; half filled: from [30]

matched systems whereas the lower barrier values correspond to disordered interfaces [17, 18]. We have also included data of $Pd_2Si$ and PtSi of Freeouf et al. [29, 30] both characterized by slightly higher work functions than ours. Besides our results these are the only known $\phi_B - W$ couples to date for silicides. It must be kept in mind that barriers $\phi_B$ are, in most cases, measured by a reaction of transition metal films on single crystal wafers whereas our work functions $W$ are averaged values over all crystallographic directions. To be strict one should also plot averaged $\phi_B$ values, which is too laborious a task. The second alternative is to measure work functions of single crystal silicides, as grown on single crystal silicon. The latter solution is only possible for perfectly lattice matched systems which is the exception rather than the rule. With this weakness in mind we will discuss our results plotted in Fig. 2.

It is tempting to consider two groups of silicides: group I containing barrier values between 0.57 and 0.71 eV involving Cr, Ti, V, Co, Mo, W, Ni, Pd as silicide-forming transition metals. The scatter in $\phi_B$ of 11% is obviously larger than in $W$(1.4%). This point will be discussed below. Group II involves the noble metals Os, Ir, Pt, Pd, and Ni. The latter is inferred from the high barrier value of lattice matched $NiSi_2$ ($\phi_B \simeq 0.79$ eV) [17, 18] and NiSi ($\phi_B \simeq 0.78$ eV) [18]. If unmatched both values drop to about 0.65–0.66 eV [17, 18]. A least square fit for the first group leads to $\phi_B = -0.26 + 0.19\, W$ (with $\phi_B$ and $W$ in units of eV) whereas with the presently available data it does not seem to make sense to correlate the high $\phi_B$'s and $W$'s for group II noble metal silicides. The initial driving force to our study was an attempt to explain deviations in the Andrews-Phillips plot by anomalously high work functions of some transition metal silicides exhibiting very high barriers $\phi_B$ with n-Si. Obviously, our results appear to give a negative answer to this question. Perhaps this is not too surprising in view of many other unsuccessful attempts to correlate $\phi_B$ with other physical properties [2]. From empirical studies we can simply state that the highest barriers on n-Si can be expected in contact with noble metals and noble metal silicides, or perhaps also other noble metal compounds with relatively strong electronegative ligands such as HgSe, $(SN)_x$, $Ag_2F$, $RuO_2$, $IrO_2$, $OsO_2$, $Rh_2O_3$, $PtO_2$, $ReO_3$ or corresponding sulfides, borides etc.

At present, the empirical study published by Schmid [1] appears to be the most successful and most satisfactory to experimentalists in relating the barrier height to Miedema's electronegativity of elemental metals. Also when one takes into account the interface density of states due to variable lattice mismatch between silicon and its silicides. This is in particular suggested from the case study of $NiSi_2$ [17] and NiSi [18] mentioned above. Other examples for large barriers of lattice matched systems are available such as HgSe/CdSe [20] HgTe/CdTe and probably also $Pd_2Si$ [29, 31]. In 5*d*-noble metal systems, however, such as PtSi, IrSi, and $IrSi_3$, with a lattice mismatch near 10% or more, barrier heights are nevertheless higher than with any other metals and roughly independent of composition of silicides. Together with our findings that work functions for the 5*d*-noble metal silicides are irrelevant we may conclude surprisingly that elemental parameters such as electronegativities and work functions appear to correlate better than the relevant electronic parameters of silicides. Lattice mismatch may account for deviations as large as 20%, as concluded by Tung's [17] and Liehr et al.'s [18] experiments.

The puzzling questions about the uncorrelated group II high $\phi_B$ values remain, however, unsolved. Andrews and Phillips [6] argued that their only anomaly (PtSi), at that time, may be due to an ordered Pt/Si interface where an electron transfer may take place to interface states arising from an ionic Pt–Si bond. This would reduce the effective interface density of states $D_i$ and practically have the same effect as perfect lattice matching, e.g. as in NiSi, $NiSi_2$. This possible explanation was inferred from a particular structural consideration of PtSi. In view of many other structural types IrSi, $Pt_2Si$, $IrSi_3$, $OsSi_2$, this explanation may not represent the full truth. The question about interface states in group I and group II is particularly intriguing. A study of electron transfer by high resolution XPS or UPS of Si interface atoms may be able to resolve this problem. Are interfaces of group II silicides with n-Si particularly characterized by low $D_i$ values or if not can $\phi_B$ of group II possibly be increased further by reducing $D_i$? For the time being this question remains unanswered.

In addition to Schmid's studies, similar correlations have been found previously by Tove [32], Donoval et al. [33] for silicon, Morgan and Frey [34] for III–V's and II–VI's, and Champness and Chan [35] for selenium in which elemental work functions or Pauling's electronegativities were used. The latter are expected to be linearly correlated so there is no basic difference when the barrier is correlated with either quantity [36].

Freeouf [30] has also studied the relationship between $\phi_B$ of tm-Si/n-Si and elemental parameters by "defining" a work function $W_{nm}$ of a tm-silicide $Si_nM_m$ as: $W_{nm} \equiv (W_{Si}^n W_M^m)^{\frac{1}{n+m}}$. For $W_{Si}$, a value of $\chi_{Si} + Eg/2 = 4.40$ eV was chosen. Remarkably, for two of his quoted experimental values (for $Pd_2Si$ and PtSi) his hypothetical values are close to experimental

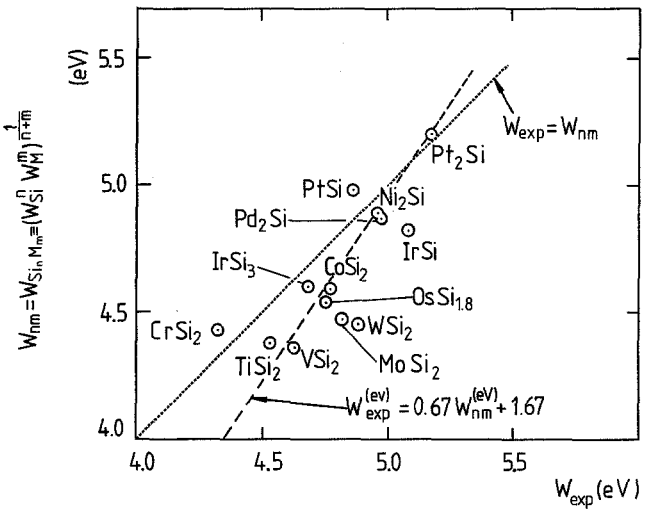


Fig. 3. Hypothetical work functions [30] vs. experimental work functions of transition metal silicides as determined from photoemission experiments

values. We have extended this relationship and plotted all existing values $W_{exp}$ vs. $W_{nm}$ defined above in Fig. 3. This plot is possibly of some interest to evaluate work functions from elemental parameters because a general theory for work functions in intermetallics has not been worked out yet. A least square's fit yields

$$W_{exp}^{(eV)}=0.67\ W_{nm}^{(eV)}+1.67\,. \tag{1}$$

The latter is larger than expected from PtSi and $Pd_2Si$ only.

Finally, returning to our correlation of group I silicides we find that our results with silicides

$$\phi_B=C_2W+C_3 \tag{2}$$

are close to similar cases, e.g. $M$/n-Si, $M$ being a metallic element. for $M$/n-Si [7] gives: $\phi_B=0.27\,W-0.55$ whereas from Fig. 2 we find $\phi_B=0.19\,W-0.26$. From $C_2$ and $C_3$ we may derive the interface density of states $D_i$ and $\phi_0$, the position of the neutral level. Using Sze's notation for $M$/n-Si systems [7] we find for $D_i$ and $\phi_0$

$$D_i\simeq 1.1\times 10^{13}\,\frac{1-C_2}{C_2}\simeq 4.7\times 10^{13}\ \mathrm{cm^{-2}eV^{-1}} \tag{3}$$

and

$$\phi_0=E_g-\frac{C_2\chi_{Si}+C_3+\Delta\phi}{1-C_2}\simeq 0.44\,\mathrm{eV}\,. \tag{4}$$

Both values are somewhat larger than in $M$/n-Si barriers where values of $3\times 10^{13}\,\mathrm{cm^{-2}eV^{-1}}$ and $\phi_0=0.32\,\mathrm{eV}$ are obtained. We may conclude that Schottky barriers between n-Si and metals are not significantly different from n-Si/silicides.

## 3. Conclusion

1) The low barrier tm-Si/n-Si values appear to correlate linearly with the work functions of tm-Si. The correlation is comparable to metallic elements resulting in similar values for the interface density of state $D_i$ and neutral level $\phi_0$.

2) Barriers with noble metal silicides do not appear to correlate with their work functions. Barrier values appear to saturate between 0.9–0.95 eV irrespective of lattice match problems.

3) Our experimental values of work functions of $Si_nM_m$, $M$ being a transition element, correlate reasonably well with Freeouf's hypothetical values $W_{nm}\equiv(W_{Si}^n W_M^m)^{\frac{1}{n+m}}$.

## 4. Outlook

1) For the search of high-barrier systems other n-Si/noble metal silicides would be interesting, in particular with 5*d*-noble metals. The question of increasing barriers to even higher values in 5*d*-noble metal silicides by lattice matching should be investigated further.

2) More data of other 5*d*-noble metal silicides would be very desirable to confirm our conclusions possibly further, but also an extension on the lower barrier side to metals with lower electronegativities (Mg, rare earths etc.) would be of interest.

3) A more detailed interface analysis of electron transfer between transition metals and silicon by XPS or UPS would be also invaluable for a better understanding of the present results.

4) The study of MIS structures with various 5*d*-noble metal silicides would be also of considerable value for device application.

*Acknowledgements.* We are very much indebted to M. Schlüter and T.M. Rice for many valuable comments.

## References

1. P.E. Schmid: Helv. Phys. Acta **58**, 371 (1985)
2. S. Krawczyk, P. Viktorovitch: Thin Solid Films **111**, 1 (1984)
3. R.H. Williams: Contemp. Phys. **23**, 329 (1982)
4. M. Schlüter: Thin Solid Films **93**, 3 (1982)
5. P.S. Ho: J. Vac. Sci. Technol. A**1**, 745 (1983)
6. J.M. Andrews, J.C. Phillips: Phys. Rev. Lett. **35**, 56 (1975)
7. For a review see: S.M. Sze: *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York 1981), Pt. III, Chap. 5
8. S.P. Murarka: J. Vac. Sci. Technol. **17**, 775 (1980)
9. See also particular references given in Table 1 which are more recent than [7, 8]
10. S.P. Murarka: Mat. Lett. **1**, 26 (1982)
11. G. Ottaviani: J. Vac. Sci. Technol. **16**, 1112 (1979)
12. G. Ottaviani, K.N. Tu, J.W. Mayer: Phys. Rev. Lett. **44**, 284 (1980)

13. C.H.P. Lupis: *Chemical Thermodynamics of Materials* (Elsevier, Amsterdam 1983) Chap. VIII
14. A.R. Miedema: J. Less.-Common Met. **46**, 67 (1976) A.R. Miedema, R. Boom, F.R. de Boer: J. Less-Common Met. **41**, 283 (1975)
15. A.M. Cowley, S.M. Sze: J. Appl. Phys. **36**, 3212 (1965)
16. B. Studer: Solid State Electron. **23**, 1181 (1980)
17. R.T. Tung: Phys. Rev. Lett. **52**, 461 (1984)
18. M. Liehr, P.E. Schmid, F.K. LeGoues, P.S. Ho: Phys. Rev. Lett. **54**, 2139 (1985)
19. R.T. Tung, J.M. Gibson: J. Vac. Sci. Technol. A**3**, 987 (1985)
20. J.S. Best, J.O. McCaldin: J. Vac. Sci. Technol. **16**, 1130 (1979)
21. S. Schulz: Diplomarbeit, Universität Konstanz (Februar 1984)
22. P. Munz, R. Schultheiss: Helv. Phys. Acta **57**, 769 (1984)
23. E. Bucher, P. Munz, M.Ch. Lux-Steiner, I. Frankowski: 1st Prog. Rept. to BMFT project 03E-8453A Universität Konstanz (Januar 1985) (unpublished)
24. E. Bucher, P. Munz, J. Hönigschmid, H.U. Finzel, U. Elrod, F. Greuter: *Statusbericht, Sonnenenergie* II (VDI-Verlag, Düsseldorf 1980) p. 1077
25. C.S. Petersson, J.E.E. Baglin, J.J. Dempsey, F.M. d'Heurle, S.J. La Placa: J. Appl. Phys. **53**, 4866 (1982)
26. T. Siegrist, F. Hulliger, G. Travaglini: J. Less-Common Met. **92**, 119 (1983)
27. H.B. Michaelson: J. Appl. Phys. **48**, 4729 (1977)
28. R.H. Fowler: Phys. Rev. **38**, 45 (1931)
29. J.L. Freeouf, G.W. Rubloff, P.S. Ho, T.S. Kuan: Phys. Rev. Lett. **43**, 1836 (1979)
30. J.L. Freeouf: Solid State Commun. **33**, 1059 (1980)
31. F. Herman, F. Casula, R.V. Kasowski: Physica B**117/118**, 837 (1983)
32. P.A. Tove: Surf. Sci. **132**, 336 (1983)
33. D. Donoval, L. Stolt, H. Norde, J. de Sousa Pires, P.A. Tove, C.S. Petersson: J. Appl. Phys. **53**, 5352 (1982)
34. D.V. Morgan, J. Frey: J. Appl. Phys. **52**, 5702 (1981)
35. C.H. Champness, A. Chan: J. Appl. Phys. **57**, 4823 (1985)
36. H.B. Michaelson: IBM J. Res. Devel. **22**, 72 (1978)
37. R.D. Thompson, K.N. Tu: Thin Solid Films **93**, 265 (1982)
38. M. Eizenberg, K.N. Tu: J. Appl. Phys. **53**, 6885 (1982)
39. P.S. Ho: J. Vac. Sci. Technol. A**1**, 745 (1983)
40. K.N. Tu, R.D. Thomson, B.Y. Tsaur: Appl. Phys. Lett. **38**, 626 (1981)
41. P.A. Psaras, R.D. Thomson, S.R. Herd, K.N. Tu: J. Appl. Phys. **55**, 3536 (1984)
42. G. Ottaviani, K.N. Tu, J.W. Mayer: Phys. Rev. B**24**, 3354 (1981)
43. H. Norde, J. de Sousa Pires, F. d'Heurle, F. Pesavento, S. Petersson, P.A. Tove: Appl. Phys. Lett. **38**, 865 (1981)
44. C.Y. Wei, W. Tantraporn, W. Katz, G. Smith: Thin Solid Films **93**, 407 (1982)
45. A.W. Searcy, L.N. Finnie: J. Am. Ceram. Soc. **45**, 268 (1962)