

Thin Films: The Relationship of Structure to Properties

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METAL-GERMANIUM CONTACTS AND GERMANIDE FORMATION

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ABSTRACT

In this study, we survey germanide formation and characterize Schottky-barrier properties for a number of representative metals on Ge (Al, Ag, Au, Er, Ni, Pd, Pt, Ta and Ti). It is found that the germanide formation characteristics (sequence of phase formation, kinetics, moving species) are similar to those of the corresponding silicides. The Schottky-barrier heights, however, are all similar and centered around 0.59 eV and are relatively insensitive to the metallization.

INTRODUCTION

Germanium technology is being reconsidered for detector systems and integrated circuits due to germanium's high electron mobility and very low carrier freeze-out temperatures. Optimal implementation of this technology will require an understanding of metal-germanium interactions from both metallurgical and electrical standpoints. If reactions and their subsequent impact on device characteristics can be anticipated before contact fabrication, increased device reliability and reproducibility will result. Compared to the extensive studies of silicide formation and metal-silicon Schottky contacts [1, 2], germanide formation and metal-germanium contacts have received relatively little attention [3-8]. Thus, the objective of this investigation is to survey germanide formation and to characterize Schottky-barrier contact properties for a number of representative metals. It is our intention to compare our results with those of the corresponding metal-silicon systems to expose any parallels which may exist. We have chosen metals that form simple eutectics with Ge (Al, Ag and Au) and metals that form compounds with Ge, both at low temperatures (Ni, Pd and Pt) and at high temperatures (Ta and Ti). We also include the rare-earth metal Er in our study since it is known that Er forms a very low barrier height on n-type Si[9].

EXPERIMENTAL PROCEDURE

Metallurgical reactions and electrical device characteristics were investigated with parallel sets of samples. The Ge substrates were <100> oriented and were doped to be n-type with $Sb(2 \times 10^{15} \text{ cm}^{-3})$. The wafers were first cleaned ultrasonically in acetone and in isopropyl alcohol, and then rinsed in doubly distilled H_2O . Next, the wafers were etched in $HNO_3:HF:H_2O$ (3:1:28 by volume) for 10 seconds, rinsed again in H_2O , and dipped in 10% HF until completely hydrophobic, rinsed again in H_2O and then dried with N_2 . Immediately after cleaning, the wafers were loaded into an oil-free electron-beam evaporation system. For electrical device characterization, 1 mm diameter diodes were formed on the substrates by evaporation through a mechanical mask. The base pressure prior to evaporation was about 1.0×10^{-8} Torr. Between 500A and 1200A of a metal film (Al, Ag, Au, Er, Ni, Pd, Pt, Ta or Ti) was deposited in an ambient of between 4.0×10^{-8} and 1.0×10^{-6} Torr at a rate of 5-15 Å/sec. For

determination of the moving species, 5-10 Å of W or Mo was deposited before the metal film deposition. The samples were then diced and loaded into a quartz-tube vacuum annealing furnace. Each sample was annealed at between 230°C and 800°C for 30 minutes (except for moving species investigation).

Metallurgical reactions were investigated by 3.2 MeV $^4\text{He}^{++}$ Rutherford backscattering spectrometry and glancing angle x-ray diffraction (Cu K α radiation, Read camera). Diodes were characterized by standard current-voltage measurements.

RESULTS AND DISCUSSION

Sequence of Phase Formation, Formation Temperature, and Crystal Structure

Metal/semiconductor thin film systems usually display only one phase at a time while binary phase diagrams show many possible phases. Walser and Bene [10] have proposed a rule to predict the first phase formed based on information contained in equilibrium binary phase diagrams. For metal/Si systems, the rule is about 80-90% successful. For metal/Ge systems, Wittmer, et al. [6] has found that the W-B rule is successful in predicting the first phase formed for Co, Hf, Mn, Ni and Rh on Ge and unsuccessful in the case of Pd on Ge. After the complete formation of this first phase, the next phases formed can sometimes be predicted by a rule proposed by Tsaur, et al., [11] which is also based on binary phase diagrams. The question may then be asked: can these rules be applied to predict the complete sequence of germanide formation?

The predicted and observed sequence of phase formation, crystal structure, and formation temperatures for the metal/Ge systems investigated in this study are given in Table I. For comparison, the corresponding metal/Si systems are also listed. It is found that the W-B and Tsaur rules are obeyed in only some cases. Because both prediction rules require reference to an equilibrium binary phase diagram, predictions cannot be made for those metal/Ge systems for which no phase diagram exists. Even so, it is important to note that, in all cases, there is a one-to-one correspondence between first and second phase formation in metal/Ge systems and metal/Si systems regardless of the success of the phase sequence prediction schemes. One reason for the failure of the rules in metal/Ge cases and success in the corresponding metal/Si cases, is the fact that the phase diagrams for the two systems may not correlate exactly. Thus, the sequence of phase formation may be predicted for other metal/Ge systems by direct inference from the corresponding metal/Si systems.

Growth Kinetics and Moving Species for Near-Noble Metal Germanides

The observed dependence of thickness on anneal time and the growth rate activation energy for Ni_2Ge , Pd_2Ge and Pt_2Ge are shown in Table II. For comparison, data for the corresponding silicides are given. All of these near-noble metal compounds show a square-root dependence, hence all reactions are diffusion-limited. In addition, activation energies of corresponding germanides and silicides are found to be about the same.

Table II lists the moving species observed in this study (with the indicated marker) for Ni_2Ge , Pd_2Ge and Pt_2Ge . The metal is seen to move for Ni_2Ge , Ni_2Si , Pt_2Ge , and Pt_2Si formation. In the cases of Pd_2Ge , both

Table 1. Comparison of observed sequence of phase formation, crystal structure and typical formation temperature for germanide formation with those for silicide formation.

Phase Sequence Predicted	observed	Germanide	Crystal Structure	Typical Formation Temp., [°C]	Phase Sequence		Silicide	Crystal Structure	Typical Formation Temp., [°C]
					Predicted	Observed			
1st	1st	Ni ₂ Ge	Orthorhombic Ni ₂ Si	~250	1st	1st	Ni ₂ Si	Orthorhombic Ni ₂ Si	200-350
2nd	2nd	NiGe	Orthorhombic MnP	260-600	2nd	2nd	NiSi	Orthorhombic MnP	350-750
					3rd	3rd	NiSi ₂	Cubic CaI ₂	>750
1st	1st	Pd ₂ Ge	Hexagonal Fe ₂ P	~230	1st	1st	Pd ₂ Si	Hexagonal Fe ₂ P	100-300
2nd	2nd	PdGe	Orthorhombic MnP	230[1,1]-600	2nd	2nd	PdSi	Orthorhombic MnP	850
1st	1st	Pt ₂ Ge	Hexagonal Fe ₂ P	250	1st	1st	Pt ₂ Si	Tetragonal CuAl ₂	200-500
2nd	2nd	PtGe	Orthorhombic MnP	260-300	2nd	2nd	PtSi	Orthorhombic MnP	300
3rd	3rd	Pt ₂ Ge ₃	Orthorhombic MnP	400					
4th	4th	PtGe ₂	Orthorhombic CaCl ₂	500-600					
γ[3]	1st	Ta ₂ Ge	Hexagonal CrSi ₂	700-800	γ[2]	1st	TaSi ₂	Hexagonal CrSi ₂	650
γ(3)	1st	Ti ₅ Ge ₃	Hexagonal Mn ₅ Si ₃	500	?	?	Ti ₅ Si ₃	Hexagonal Mn ₅ Si ₃	-
2nd	2nd	TiGe	Orthorhombic TiSi	600	?	?	TiSi	Orthorhombic FeB	500
3rd	3rd	TiGe ₂	Orthorhombic TiSi ₂	700-800	1st	1st	TiSi ₂	Orthorhombic	600
1st	-	Er ₅ Ge ₃	Hexagonal Mn ₅ Si ₃		γ[3]	1st	ErSi _{2-n}	Hexagonal AlB ₂	~380
1st	1st	ErGe _{2-n}	Hexagonal AlB ₂	~330					

[1] Pd₂Ge and PdGe are found to coexist at intermediate temperatures.

[2] W-B rule not conclusive from phase diagram - two equal temperature eutectic points.

[3] No phase diagram available.

Pd and Ge are seen to move. In the case of Pd₂Si formation, both Pd and Si have been seen to move, although this point may be controversial.[12]

Table II. Comparison of the experimentally observed dependence of grown thickness on anneal time (t), activation energy, and moving species (marker in parentheses) for near-noble metal germanide formation with established data for silicide formation.

Compound	Ni ₂ Ge	Ni ₂ Si	Pd ₂ Ge	Pd ₂ Si	Pt ₂ Ge	Pt ₂ Si
Grown Thickness α	$\sqrt{t}$	$\sqrt{t}$	$\sqrt{t}$	$\sqrt{t}$	$\sqrt{t}$	$\sqrt{t}$
Activation Energy (eV)	1.6	1.5	1.08	~1.0	1.3	1.5
Moving Species	Ni (W)	Ni	Both (W)	Si and/or Pd	Pt (Mo)	Pt

SCHOTTKY BARRIERS

In view of the fact that a given metal will have the nearly same reaction behavior in both the Ge and Si systems, the question arises as to whether the Schottky barriers formed at metal/Ge interfaces depend on the metal in a corresponding way to those at metal/Si interfaces. Some similarities may be expected due to the isoelectronic nature of the two semiconductors. In this study, the dependence of barrier height for metals on n-type Ge has been investigated. The results for as-deposited samples are plotted in Fig. 1, where the effective Richardson constant is assumed to be 142.8 A/cm²/K². [15]

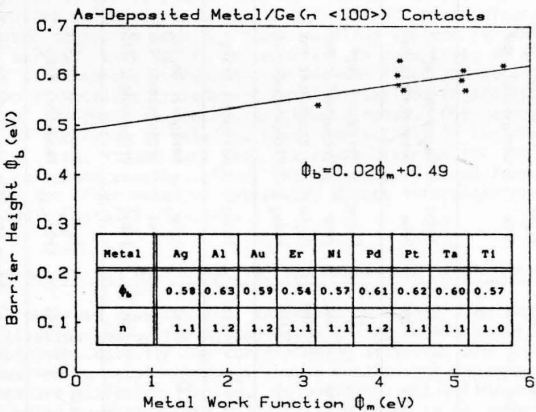


Figure 1. Barrier heights of as-deposited metal/Ge diodes plotted against metal work function. The line is a least square fit to the data.

A least squares fit to our data yields the relation:

$$\phi_b = 0.02\phi_m + 0.49 \text{ eV.} \quad (1)$$

Clearly, the barrier height is nearly independent of the metal, contrary to the Schottky [13, 14] model. These results are in agreement with those of Chan and Card [8] who found that the barrier heights of Au, Cu, Ni and Ag on Ge(n, <111>) center around 0.54 eV with a standard deviation of only 0.04 eV. From Table III, it can be seen that the barrier heights remain unchanged even after germanide formation.

Table III. Schottky barrier heights and ideality factors, n (in parentheses), for as-deposited metal/Ge ($n, <100>$) contacts determined by I-V measurements at room temperature.

Metal(M) Contact	Er	Ni	Pd	Pt	Ta	Ti
M/Ge	0.54(1.1)	0.57(1.1)	0.61(1.1)	0.62(1.1)	0.60(1.1)	0.57(1.0)
M ₂ Ge/Ge	-	0.58(1.2)	0.61(1.1)	0.61(1.1)	-	-
MGe/Ge	-	0.59(1.1)	0.61(1.1)	0.62(1.1)	-	0.60(1.1)
MGe ₂ /Ge	~0.52(1.1)	-	-	0.62(1.1)	ohmic	ohmic

The non-ideality of the diodes ($n \geq 1.1 - 1.2$) may be due to the fact that minority carrier injection must also be considered for high barrier heights ($\phi_b \sim E_g$) in addition to majority carrier thermionic emission.[17] After formation of TaGe₂ and TiGe₂ these contacts become ohmic. Optical microscopy reveals that surface morphology of these samples is not smooth, indicative of a non-planar interface. This is consistent with a model by Nicollian and Sinha [18] who have pointed out that an ohmic contact may result if the width of the metallurgical junction is greater than the width of the depletion region.

With regard to the elements Al, Ag and Au, which do not form compounds with Ge, at annealing temperatures where interactions between the metal and Ge become detectable by Rutherford backscattering spectrometry, the Au and Ag contacts become ohmic in nature whereas the Al contacts remain rectifying and unchanged. This behavior may stem from the fact that Au and Ag present deep levels in Ge whereas Al is a shallow acceptor.

Attempts were made to correlate the observed barrier heights with physical parameters according to various models [13]. None of the correlations (e.g., effective metal work function, metal electro-negativity, eutectic temperature) succeeded.

According to the Bardeen model [19], the quantity of surface states necessary to pin the Fermi level to the experimentally observed degree may be calculated. Thanailakis and Northrop [7] applied an equation developed by Cowley and Sze [14] to calculate the density of states for metal/Ge contacts to be $2 \times 10^{13} \text{ eV cm}^{-2}$ assuming an interfacial oxide thickness of 20Å. In this study, we checked for an interfacial oxide layer at the Pd/Ge and Ta/Ge interfaces with $^{16}\text{O}(d, \alpha)^{14}\text{N}$ nuclear reaction spectrometry and found none within the resolution of the measurement ($\sim 3\text{Å}$). Thus, this model cannot be applied in this case. Nevertheless, the barrier heights observed in this study are consistent with the Fermi level pinning for metal/Ge contacts found by authors using various theories and experimental techniques.[20-22]

CONCLUSION

We have shown that direct parallels exist between the formation characteristics of germanides and silicides. For all systems studied, the sequence of phase formation, the kinetics, and the moving species are the same. Thus, predictions for new metal/Ge systems may be made based on knowledge from the corresponding metal/Si systems. In contrast, the barrier heights of metal (germanide)/Ge contacts were found to be less sensitive to the metallization than those of metal/Si and silicide (silicide)/Si contacts.

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