JOURNAL OF MATERIALS SCIENCE **33** (1998) 379–384

Interactions of thin films of Pd and Pd/Si on GaAs: an X-ray photoelectron spectroscopic study combined with a thermodynamic analysis

HIROAKI IWAKURO*, TSUKASA KURODA[§], DIAN HONG SHEN[§], HIDEICHI YAGI[§]
Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki 567, Japan

Interfacial reactions of Pd and Pd/Si films on [0 0 1]-oriented GaAs substrates have been studied by X-ray photoelectron spectroscopy. In the as-deposited Pd/GaAs system, Pd interacts with Ga and the As is isolated. A Pd–Ga–As compound is observed to form under the Pd–Ga and As layers. Annealing the Pd/GaAs system at 450 °C leads to the formation of islands composed of Pd–Ga and Pd–As, amongst which a Pd–Ga–As compound forms. In the Pd/Si/GaAs system, Pd diffuses in to the GaAs substrate, the Pd–Ga and Pd–Ga–As compounds are formed. In the 450 °C-annealed Pd/Si/GaAs system, little interfacial reaction at the GaAs substrate occurs. Possible interfacial reactions in the Pd/GaAs and Pd/Si/GaAs systems, including the previously investigated Pt/GaAs, Pt/Si/GaAs, Ni/GaAs and Ni/Si/GaAs systems are considered by calculation of the change in enthalpy of the reactions. The thermodynamic analyses agree with the experimental results.

1. Introduction

The development of GaAs technology has highlighted the importance of characterizing and understanding its interface with metals. Metal–GaAs junctions are used for ohmic and rectifying contacts in various devices and during processing they are subject to high-temperature cycles, which lead to interdiffusion and compound formation that can change the electrical properties of these junctions. Therefore systematic studies of the metallurgical and electrical properties of various metals on GaAs is recognized as being an extremely important area of research.

Two of the present authors have previously reported that Pt interacts with GaAs at room temperature to form a Pt-rich Pt–Ga compound and isolated As, and that the As-atoms subsequently react at 200 °C to produce $PtAs_2$ [1, 2]. They have also shown that Ni on GaAs behaves in a similar manner to Pt, and that in the Ni/Si/GaAs system a Ni-silicide formed by intermixing prevents Ga- and As-atoms from out-diffusion to the surface [3]. As for the interaction of Pd with GaAs it has been reported by Olowolafe *et al.* [4] and Zeng and Chung [5], that compounds of Pd with Ga or As are formed at temperatures higher than 250 °C. Recent reports [6, 7] have indicated, however, that in the first stage of the reaction Pd–Ga–As compounds are formed, the constituents of which vary depending on the experimental conditions. However the exact details about this process are still not fully understood and remain controversial.

This paper describes interfacial reactions in Pd/GaAs and Pd/Si/GaAs systems. In particular, in the latter system, attention is focussed on the chemical stability of the Pd silicides and the GaAs interface. It is a requirement for application in GaAs microelectronic devices that the metal electrodes do not strongly react with the GaAs substrate.

The as-deposited and annealed films are observed using X-ray photoelectron spectroscopy combined with Ar ion sputtering. This method is useful for in-depth monitoring of the binding energy for each element. The energy levels tend to shift during compound formation, and these shifts indicate the change in the chemical state of the constituents. In this case the Ar sputtering effects must be considered.

2. Experimental procedure

GaAs wafers, [100] oriented, p-type with a conductivity of 0.005 Ωcm, were cleaned with a solution of $3:1:1$ $H_2SO_4:H_2O_2:H_2O$ for 60 s and rinsed in H_2O to remove the native oxide before the film growth. Thin films of Pd and Si, each of 70–100 nm in thickness, were deposited onto the GaAs wafers at room temperature using a resistively heated tungsten filament. The deposited films were then annealed at

**Present address*: Shindengen Electric Mfg. Co., Ltd., 10-13 Minami, Hanno, Saitama 357, Japan
[§]*Present address*: State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Science, Bejing, The People's Republic of China

0022–2461 © *1998 Chapman & Hall*

450 °C for 30 min in a vacuum. During evaporation and annealing, the base pressure was 6.7×10^{-5} Pa.

X-ray photoelectron spectra (XPS) were obtained with a Dupont ESCA 760B instrument using an MgKα (1253.6 eV) X-ray source. The acceleration voltage and emission current of the X-ray source were 8 kV and 30 mA, respectively. The base pressure of the analysis chamber was 2.7×10^{-6} Pa during the data collection. In the depth profiling experiments the samples were sputtered with 2 keV argon ions at a current of 20 μA cm^{-2}. The samples were rotated during the sputtering to ensure uniform etching of the surface.

For comparison, Pd, PdO, Ga, Ga_2O_3, As, and GaAs were used as standard samples to determine binding energies and full widths at half maximum (FWHM's) for the Ga 3d, As 3d, Pd $2p_{3/2}$, C 1s and O 1s photoelectron spectra together with the apparent binding energy and FWHM of the Ga $L_3M_{45}M_{45}$(Ga *LMM*) Auger spectrum. The binding energy of an Auger electron refers to the energy difference between the energy of the MgK_α X-ray and the kinetic energy of the Auger electron.

For quantitative depth analysis, we determined the relative atomic sensitivity factors (ASF's). The ASF's of the Ga 3d, As 3d, Pd $2p_{3/2}$ and O1s spectra were determined from the Ga_2O_3, PdO and GaAs standard samples while that of C 1s was obtained from the work of Wagner *et al.* [8]. In addition, we have to consider the Ar ion sputtering effects for Ga, As, Pd and Si compounds if we are to correctly identify the chemical states by analysis of the binding energy and FWHM's of the photoelectron and Ga *LMM* Auger spectra. For chemically etched GaAs, the Ga 3d, As3d, and Ga *LMM* Auger peaks were observed to occur at binding energies (FWHM's) of 18.8 (1.3), 40.8 (1.6), and 186.7 eV (2.2 eV), respectively. After the Ar ion sputtering, the Ga 3d, As 3d, and Ga *LMM* Auger peaks shifted to the binding energies (FWHM's) of 18.9 (1.5), 40.9 (1.7), and 186.9 eV (2.6 eV), respectively. The sputtered surface became Ga rich as compared to the chemically etched surface. The preferential sputtering coefficient P(As/Ga) was estimated to be about 1.2. Since the preferential sputtering coefficients for P(Pd/Ga), P(Pd/As), and P(Pd/Si) are unknown, the values were assumed to be unity. Taking the Ar ion sputtering effects into account, the resulting ASF's, were found to be 1.3 for As 3d, 0.5 for Si 2p, 5.9 for Pd $2p_{3/2}$, 0.6 for C 1s and 1.9 for O 1s with respect to Ga 3d.

The relative concentration, C_n, of element n was determined from the following equation:

$$C_n = \frac{I_n/S_n}{\Sigma I_i/S_i} \quad (1)$$

where I and S are the XPS peak intensity and the ASF's of n.

In-depth profiles will be shown in Section 3, the C and O data will not be presented because of the presence of carbon and oxygen atoms just near the sample surfaces.

The line shapes of the decomposed spectra were assumed to be the same as that for the Ga *LMM* Auger spectrum, which had a broader FWHM due to the Ar ion sputtering effects, in Ar-ion-sputtered GaAs.

3. Results and discussion

3.1. The Pd/GaAs system

Fig. 1(a–c) shows the depth profiles for the as-deposited Pd/GaAs system. The Ga *LMM* Auger spectra obtained at points A_1, B_1 and C_1 in Fig. 1c are presented in Fig. 2(a–c), respectively.

In Fig. 1b, the As 3d binding energy of 41.7 eV at the surface agrees with that for elemental As. According to Fig. 1(a and c) the binding energy of the Ga *LMM* Auger spectra, which is constant at 186.0 eV in the Pd film, increases to 187.2 eV during sputtering for 20 min, and then shifts to 186.9 eV which is the binding energy of Ga in GaAs. These results indicate that an interfacial reaction between Pd and GaAs has occurred in the as-deposited system.

The Ga *LMM* Auger spectrum at A_1 contains a single peak at 186.0 eV which can be attributed to a Pd–Ga compound. The Ga *LMM* Auger spectrum at B_1 and C_1 can be separated into two peaks at 186.3 (or 186.4) and 187.5 eV (or 187.4 eV). Though the intensity of the 186.3 eV peak is larger than that of the 187.5 eV peak at B_1, the intensity of the 187.5 eV peak is larger at C_1. This indicates that a compound corresponding to the spectrum of 187.5 eV is present at the

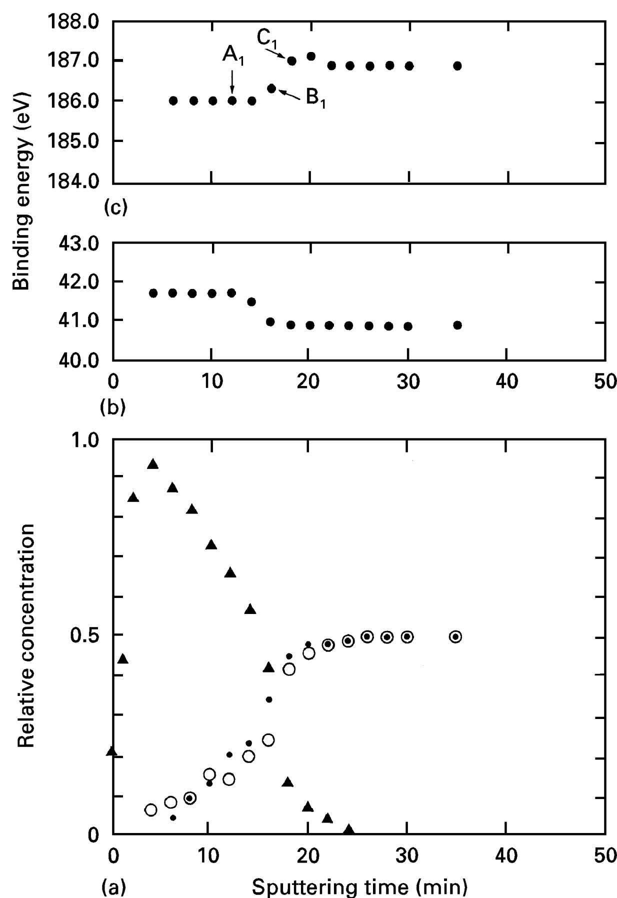


Figure 1 Depth profile in the as-deposited Pd/GaAs system: (a) relative concentration: ● Ga, (○) As and (▲) Pd; (b) As 3d peak, (c) Ga *LMM* Auger peak.

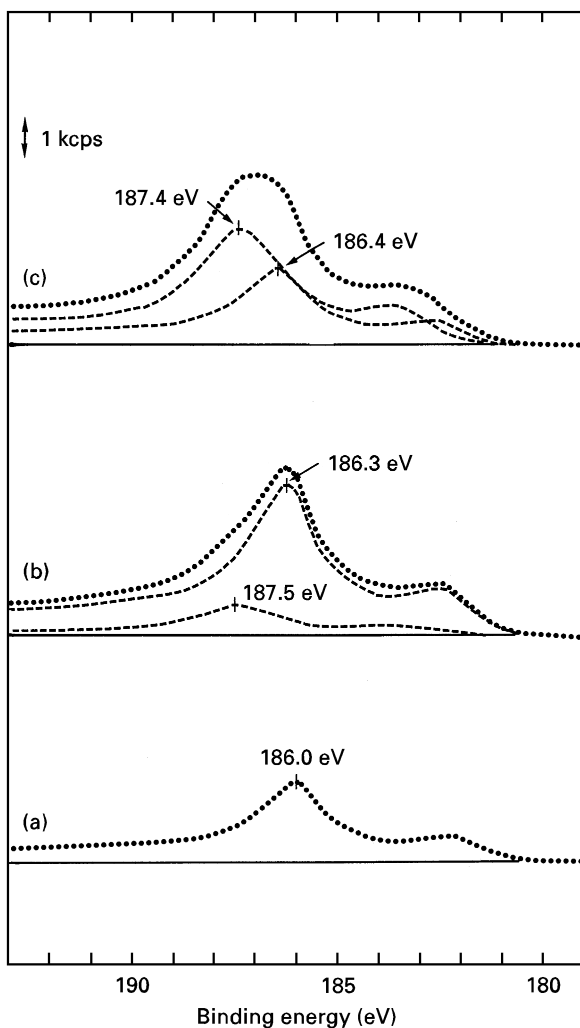


Figure 2 Ga *LMM* Auger spectra obtained at (a) A_1, (b) B_1 and (c) C_1 in Fig. 1c.

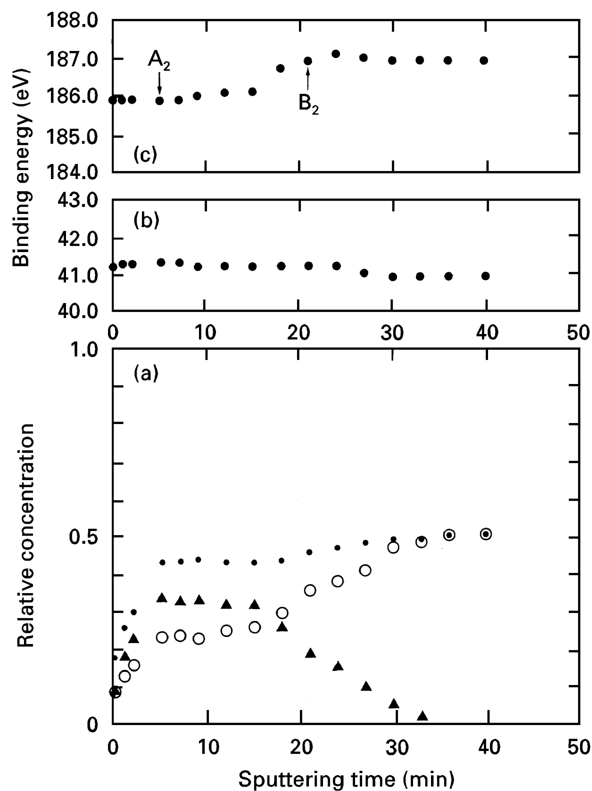


Figure 3 Depth profile in the 450 °C-annealed Pd/GaAs system: (a) relative concentration: (●) Ga, (○) As and (▲) Pd; (b) As 3d peak, (c) Ga *LMM* Auger peak.

GaAs substrate side. Previous papers on Pd/GaAs reactions have shown that Pd–Ga–As ternary compounds are formed during the initial stages of the interaction between Pd and GaAs [6, 7]. Therefore the 187.5 eV peak is attributable to a Pd–Ga–As ternary compound.

Fig. 3(a–c) shows the depth profiles in the 450 °C-annealed Pd/GaAs system. The Ga *LMM* Auger spectra obtained at A_2 and B_2 in Fig. 3c are presented in Fig. 4(a and b).

Fig. 3a indicates that the distribution of Ga is nearly uniform in the Pd film. This behaviour is similar to those obtained in the 450 °C-annealed Pt/GaAs and Ni/GaAs systems [1, 3], in which island formation occurred.

The Ga *LMM* Auger spectrum at A_2 can be separated into two spectra with peaks at 185.9 and 187.4 eV. These spectra can be attributed to Pd–Ga and Pd–Ga–As compounds, respectively, which are observed at the near substrate region B_2. This is clear evidence for island formation [1].

In Fig. 3b, the As peak at the surface side appears at 41.2 eV, which differs from the binding energies for elemental As (41.7 eV) and GaAs (40.9 eV). This is due to the reaction of As to form a Pd–As compound.

3.2. The Pd/Si/GaAs system

Fig. 5(a–c) shows the depth profiles in the as-deposited Pd/Si/GaAs system. The Ga *LMM* Auger spectra obtained at A_3 in Fig. 5c are presented in Fig. 6.

As shown in Fig. 5(b and c), the Ga *LMM* Auger and As 3d peaks change by only 0.1 eV. Three spectra with peaks at 185.9, 186.9 and 187.4 eV are observed at A_3, which correspond to Pd–Ga, GaAs and Pd–Ga–As compounds, respectively. These results indicate that the reaction between the Pd/Si film and GaAs occurred in the as-deposited state.

Fig. 7(a–c) shows the depth profiles in the 450 °C-annealed Pd/Si/GaAs system. The Ga *LMM* Auger spectra obtained at A_4–C_4 in Fig. 7c are given in Fig. 8(a–c), respectively.

Fig. 7a indicates that there is intermixing of Pd and Si, resulting in the formation of Pd silicides. The change in the Ga *LMM* Auger and As 3d peaks is similar to those in the as-deposited Pd/Si/GaAs system (Fig. 5(b and c)). In the Ga *LMM* Auger spectra at A_4 and B_4, the peaks corresponding to Pd–Ga, GaAs and Pd–Ga–As compounds are observed. Comparing Fig. 7a with Fig. 5(a), we can see that the interface width is larger than that of the as-deposited system. These results indicate that the interfacial reaction occurred only slightly after annealing at 450 °C.

3.3. Thermodynamic considerations

The Gibbs free energy of a reaction is related to the enthalpy, ΔH_R, and entropy, ΔS_R, of the reaction, and

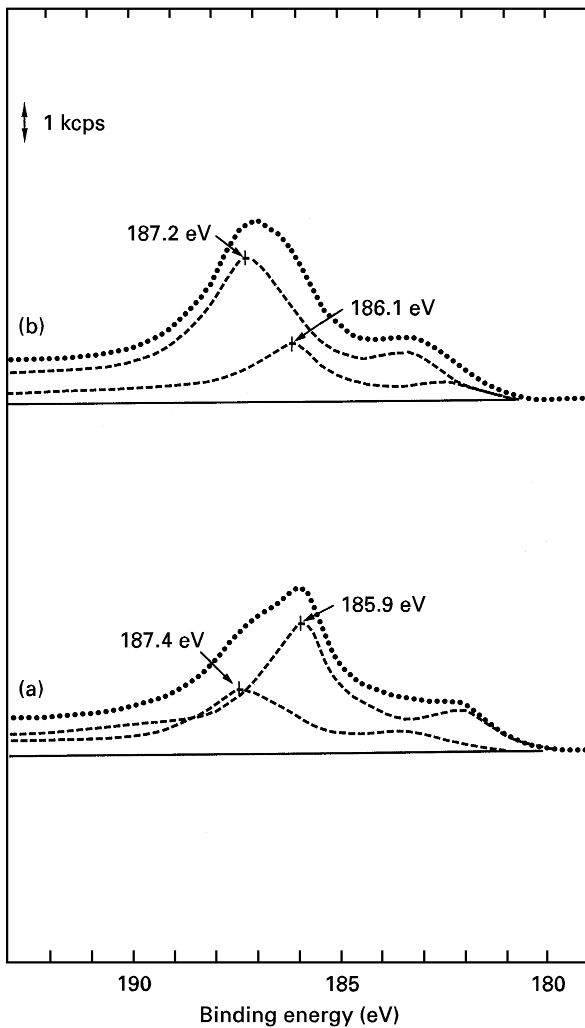


Figure 4 Ga *LMM* Auger spectra obtained at (a) A_2 and (b) B_2 in Fig. 3c.

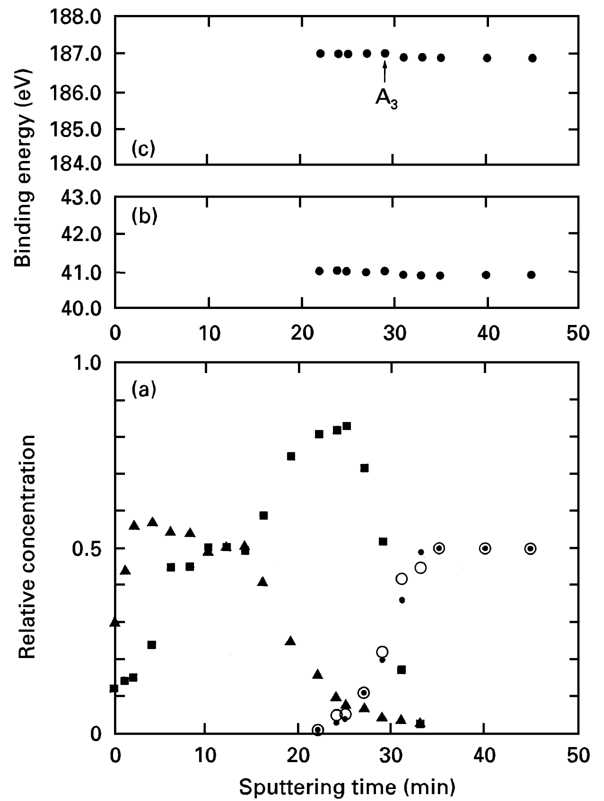


Figure 5 Depth profile in the as-deposited Pd/Si/GaAs system: (a) relative concentration (●) Ga, (○) As, (▲) Pd and (■) Si (b) As 3d peak, (c) Ga *LMM* Auger peak.

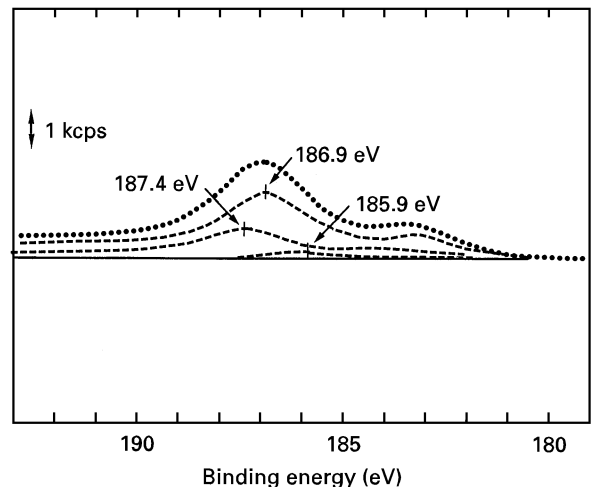


Figure 6 Ga *LMM* Auger spectra obtained at A_3 in Fig. 5c.

to the absolute temperature by the equation:

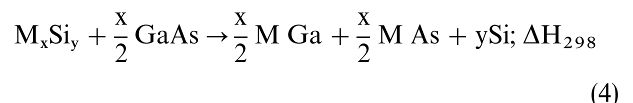
$$\Delta G_R = \Delta H_R - T\Delta S_R \tag{2}$$

Values for ΔH_R can be readily calculated from published values of the enthalpies of formation, ΔH_f, using the equation:

$$\Delta H_R = \Sigma\Delta H_r \text{ (products)} - \Sigma\Delta H_f \text{ (reactants)} \tag{3}$$

Values for ΔS_R are not available for all of the reactions and they are also less reliable than the ΔH_R values, so it is difficult to determine absolute values of ΔG_R for a complete set of reactions. Since we are primarily concerned with the relative values of ΔG_R, and noting that $T\Delta S_R$ is normally small compared to ΔH_R, ΔG_R can be approximated by ΔH_R. The ΔH_f's used in the present analysis are obtained at 1 atm (1.013×10^5 Pa) and 298 K. Table I lists these standard heats of formation ΔH_{f0}, that are used in the calculations.

We can use the free-energy change to judge whether or not a chemical reaction occurs. The contribution of entropy to the free-energy is usually small, so that the free-energy change can be approximated by the enthalpy of the heat of reaction (the difference between the heats of formation of the reaction products and the reactants). We have estimated the heat of reaction at 298 K, ΔH_{298}, for a wide variety of metal–GaAs systems using the chemical reaction:



$$M_xSi_y + \frac{x}{2}\text{GaAs} \rightarrow \frac{x}{2}\text{M Ga} + \frac{x}{2}\text{M As} + y\text{Si}; \Delta H_{298} \tag{4}$$

Several assumptions were required in the estimation of ΔH_{298}. These include (i) the reaction produced only equiatomic M–Ga and M–As compounds (M = metal) because they have small values of the heat of formation; (ii) any chemical reaction between Si and GaAs resulting in compound formation is ignored; (iii) the points that the metallization occurs in

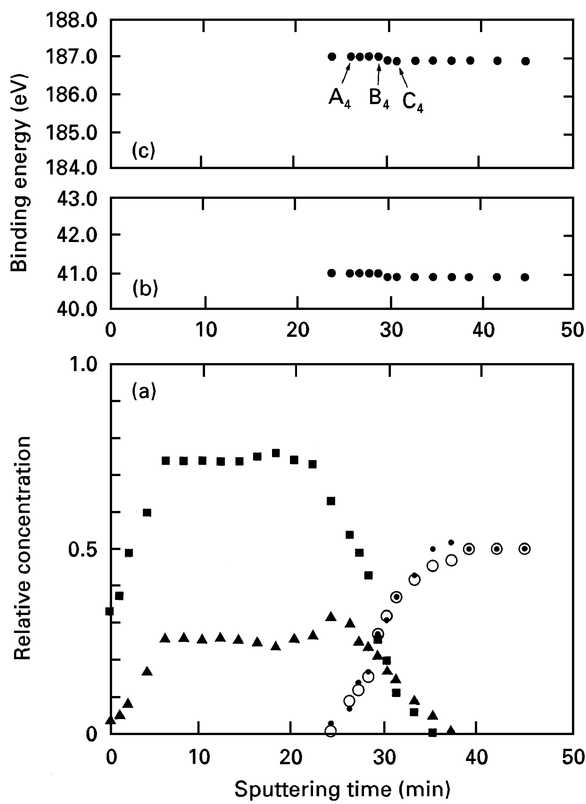


Figure 7 Depth profile in the 450 °C-annealed Pd/Si/GaAs system: (a) relative concentration (●) Ga, (○) As, (▲) Pd and (■) Si, (b) As 3d peak, (c) Ga *LMM* Auger peak.

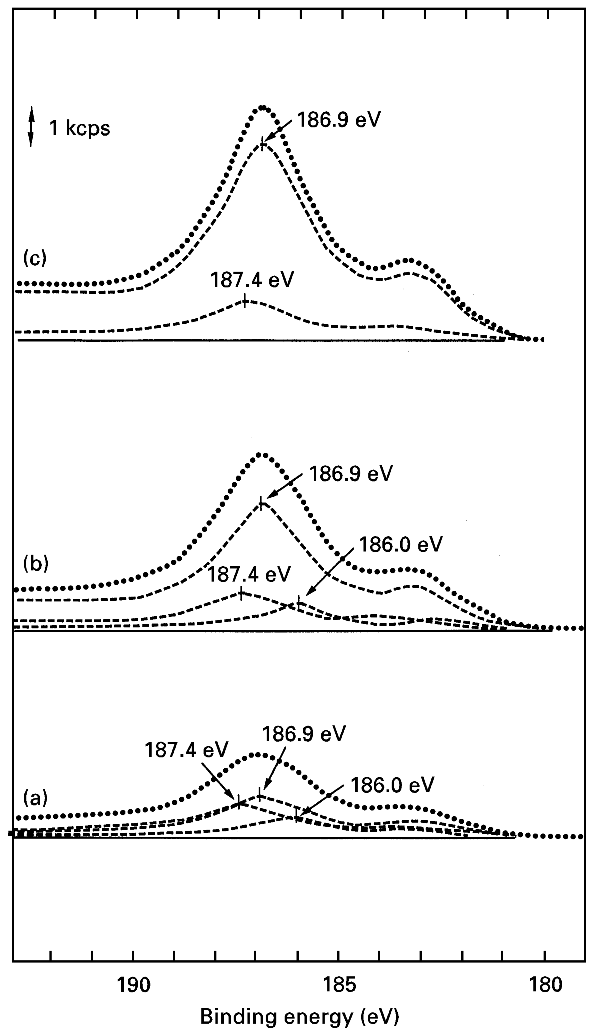


Figure 8 Ga *LMM* Auger spectra obtained at (a) A_4, (b) B_4 and (c) C_4 in Fig. 7c.

thin films and that the sample suffers from high-temperature annealing does not influence the thermodynamic results.

The enthalpy produced by a typical annealing at 450 °C (723 K) is:

$$\Delta H_{723} = \int_{298}^{723} C_{\mathrm{p}} \, \mathrm{d}T + \Delta H_{298} \qquad (5)$$

The calculated ΔH_{723} obtained from C_{p} values by Pretorius *et al.* [9] and Kubaschewski and Alcock [10] showed that its contribution to the heat of reaction is generally very small and that, most importantly, the sign of the heat reaction remains unchanged. Therefore, the room-temperature heat of reaction, ΔH_{298}, can be used to approximate ΔH_{723} for the purpose of this calculation.

We applied these thermodynamic considerations to the interfacial reactions of the Pd/GaAs and Pd/Si/GaAs systems and also to those of the Pt/GaAs, Si/Pt/GaAs, Pt/Si/GaAs, Ni/GaAs, Si/Ni/GaAs and Ni/Si/GaAs systems that we have previously studied [1–3]. Table I lists the values of the enthalpy needed for the formation of compounds, which were used in calculating the Gibbs free-energy for the reactions between metals or their silicides and GaAs. When experimental values of the enthalpy are available [9, 10], they were used, otherwise we adopted those calculated by the Miedema model [11]. The reaction formulas were written under the following conditions: (1) the Si-atom does not combine with Ga- or As-atoms [12]; (2) reaction products of Pt with GaAs are PtGa and $PtAs_2$ [13], and similarly those for Ni and Pd are NiGa, NiAs [14, 15] and PdGa, $PdAs_2$ [16], respectively; (3) silicides formed in the deposited film are Pt_2Si or PtSi [17–19], Ni_2Si, NiSi or $NiSi_2$ [17], and Pd_2Si or PdSi [17].

The Gibbs free-energy changes ΔG calculated for these formulas are listed in Table II. They are negative

TABLE I Heat of formation of the M–Ga and M–As compounds

Phase	ΔH_{298}(kJ mol^{-1})
GaAs	− 81.65
PdGa	− 158.27
$PdAs_2$	− 174.60
Pd_2Si	− 86.67
PdSi	− 57.78
PtGa	− 148.22
$PtAs_2$	− 159.11
Pt_2Si	− 86.67
PtSi	− 66.15
NiGa	− 74.11
NiAs	− 72.02
Ni_2Si	− 142.78
NiSi	− 89.60
$NiSi_2$	− 94.20

TABLE II Gibbs free energy changes for potential chemical reactions

Chemical reaction	ΔG(kJ mol^{-1})
$3Pd + 2GaAs \rightarrow 2PdGa + PdAs_2$	− 327.84
$2Pd_2Si + 4GaAs \rightarrow 4PdGa + 2PdAs_2 + 3Si$	− 482.34
$3PdSi + 2GaAs \rightarrow 2PdGa + PdAs_2 + 3Si$	− 154.50
$3Pt + 2GaAs \rightarrow 2PtGa + PtAs_2$	− 292.25
$3Pt_2Si + 4GaAs \rightarrow 4PtGa + 2PtAs_2 + 3Si$	− 324.49
$3PtSi + 2GaAs \rightarrow 2PtGa + PtAs_2 + 3Si$	− 93.79
$2Ni + GaAs \rightarrow NiGa + NiAs$	− 64.48
$Ni_2Si + GaAs \rightarrow NiGa + NiAs + Si$	+ 67.41
$2NiSi + GaAs \rightarrow NiGa + NiAs + 2Si$	+ 106.34
$NiSi_2 + GaAs \rightarrow NiGa + NiAs + 4Si$	+ 108.86

for all of the investigated reactions for the Pt–GaAs system, indicating that Pt or its silicide reacts spontaneously with GaAs. However for the Ni–GaAs system, ΔG for the reaction of Ni with GaAs is negative, but they are positive for those of Ni-silicides with GaAs. Therefore Ni-silicides do not react with GaAs. It is clear from Table II that Pd and its silicides react with GaAs. These thermodynamic arguments agree with the previously discussed experimental results.

4. Conclusions

Interfacial reactions in Pd- or Pd and Si-deposited GaAs(100) were investigated by X-ray photoelectron spectroscopy, and the results were compared with thermodynamic analyses of the enthalpy of compound formation. The experimental and theoretical results agreed on the following points. (1) When Pd is deposited onto GaAs, Pd combines with Ga and the As is isolated. Under the layer of Pd–Ga and As exists a Pd–Ga–As compound. (2) Annealing the Pd/GaAs system at 450 °C forms islands composed of Pd–Ga and Pd–As, amongst which exists a Pd–Ga–As compound. (3) In the Pd/Si/GaAs system Pd diffuses into the GaAs surface immediately after the deposition, resulting in the formation of Pd–Ga and Pd–Ga–As compounds. (4) Annealing the Pd/Si/GaAs system at 450 °C promotes little interfacial reaction activity.

Acknowledgements

We would like to thank Professor M. Sawada and Dr. K. Tanaka of the Material Analysis Center, the Institute of Scientific and Industrial Research, Osaka University, for the XPS analysis.

References

1. H. IWAKURO and T. KURODA, *Jpn. J. Appl. Phys.* **28** (1989) 223.
2. T. KURODA and H. IWAKURO, *J. Appl. Phys.* **66** (1989) 1486.
3. H. IWAKURO and T. KURODA, *Jpn. J. Appl. Phys.* **29** (1990) 381.
4. J. O. OLOWOLAFE, P. S. HO, H. J. HOVEL, J. E. LEWIS and J. M. WOODALL, *J. Appl. Phys.* **50** (1979) 955.
5. X. F. ZENG and D. D. L. CHUNG, *J. Vac. Sci. Technol.* **21** (1982) 611.
6. T. SANDS, V. G. KERAMIDAS, R. GRONSKY and J. WASHBURN, *Thin Solid Films* **136** (1986) 105.
7. Y. C. ZHAO and Z. Q. WU, *Appl. Phys. Lett.* **58** (1991) 349.
8. C. D. WAGNER, W. M. RIGGS, L. E. DAVIS and J. F. MOULDER, "Handbook of X-ray photoelectron spectroscopy", (Perkin-Elmer, Eden Prairie, MN, 1979).
9. R. PRETORIUS, J. M. HARRIS and M.-A. NICOLET, *Solid State Electron.* **21** (1978) 667.
10. O. KUBASCHEWSKI and C. B. ALCOCK, "Metallugical thermo-chemistry", 5th Edn, (Pergamon, Oxford, 1979).
11. A. R. MIEDEMA, *J. Less-Common Metals* **46** (1976) 67.
12. T. E. SHIM, T. ITOH, Y. YAMAMOTO and S. SUZUKI, *Appl. Phys. Lett.* **48** (1986) 641.
13. S. K. SINHA and J. M. POATE, in "Thin films-interdiffusion and reactions", edited by J. M. Poate, K. N. Tu and J. W. Mayer (Interscience Wiley, New York, 1978).
14. A. LAHAV, M. EIZENBERG and Y. KOMEM, *J. Appl. Phys.* **60** (1986) 991.
15. M. OGAWA, *Thin Solid Films* **70** (1980) 181.
16. T. S. KUAN, J. L. FREEOUF, R. F. BATSON and E. L. WILKIE, *J. Appl. Phys.* **58** (1985) 1519.
17. K. N. TU and J. W. MAYER, in "Thin films-interdiffusion and reactions", edited by J. M. Poate, K. N. Tu and J. W. Mayer (Interscience Wiley, New York, 1978).
18. S. DANYLUK and G. E. McGUIRE, *J. Appl. Phys.* **45** (1974) 5141.
19. P. J. GRUNTHANER, F. G. GRUNTHANER and A. MADHUKAR, *J. Vac. Sci. Technol.* **20** (1982) 680.

Received 5 August 1996
and accepted 4 August 1997