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Publication Date
1985-04-01

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April 1985

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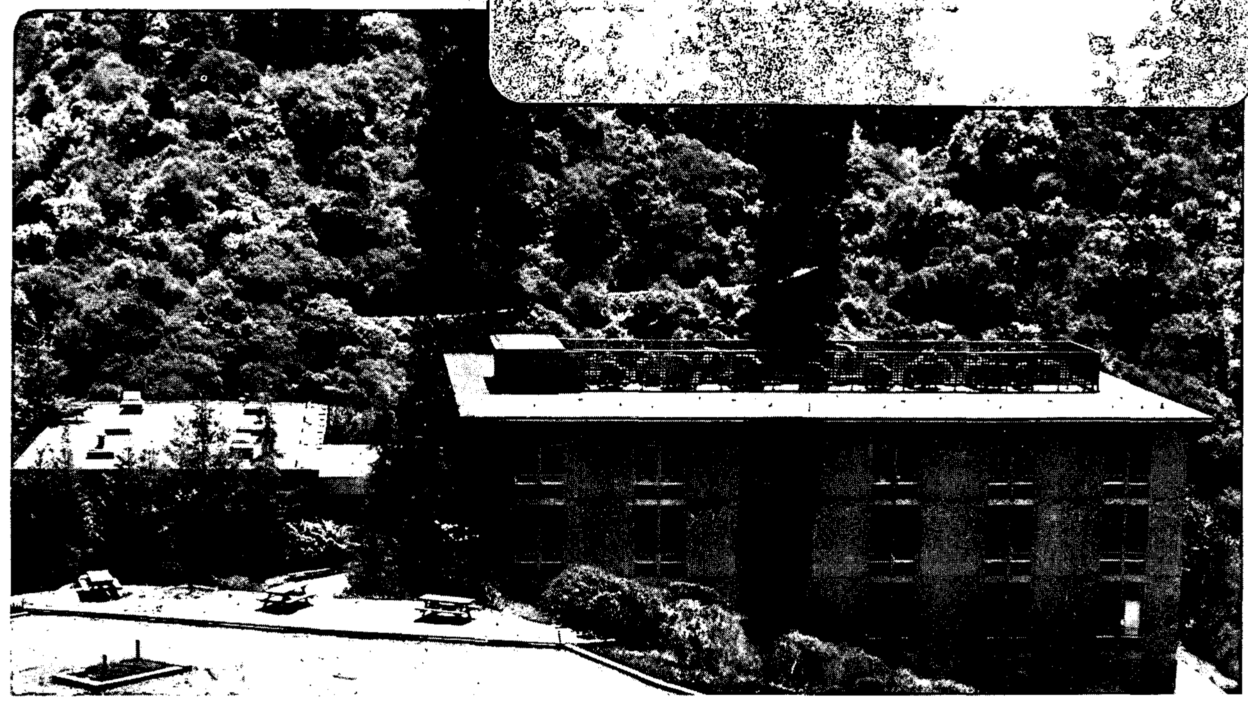

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Ternary Phases in the Pd-GaAs System: Implications for Shallow Contacts to GaAs

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ABSTRACT

Ternary phases of the type $M_xA^{III}B^V$ prepared by solid-phase reaction between a metal, M, and a substrate, $A^{III}B^V$, are potentially useful materials for forming shallow and adherent contacts to III-V semiconductors. In this letter, the results of a transmission electron microscopy study of the Pd-GaAs reaction are presented. It is shown that the first two reaction products are ternary phases of the type $M_xA^{III}B^V$ ($Pd_5(GaAs)_2$ and Pd_4GaAs). By choosing appropriate metal thicknesses and annealing temperatures, uniform monocrystalline films of $Pd_5(GaAs)_2$, free of interfacial accumulations of As and Ga, can be obtained. As contacts to GaAs, these Pd_xGaAs films are analogous to silicide contacts to silicon.

INTRODUCTION

Integration and miniaturization of III-V compound semiconductor devices necessitate the development of shallow, laterally uniform and adherent contacts. From the metallurgical perspective, potentially useful contact materials must meet several criteria: (a) The deposited metal should react with the III-V substrate to promote adhesion and this reaction must occur in the solid state if control of contact morphologies on the 10 nm scale

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is to be achieved. (b) The deposited metal should be the dominant moving species during the reaction so that voids are not formed at the contact/$A^{III}B^{V}$ interface. (c) The reaction should go to completion, resulting in a thin film of a stable ternary end phase (rich in the group III and V elements) with a composition of $M_xA^{III}B^{V}$. The principle advantage of such contacts is that their electrical and mechanical properties would not be dominated by interfacial accumulations of either group III or group V elements or by the associated nonstoichiometry of the semiconductor near the interface.

Although these criteria may be difficult or impossible to completely satisfy in practice, there is recent evidence that phases of the form M_xGaAs do exist, specifically for the metals Ni [1,2] and Pd [3,4]. Ogawa [1] and Lahav and Eizenberg [2] have shown that Ni_2GaAs is the first phase to form during annealing of Ni on GaAs. However, annealing at temperatures above 400°C results in the decomposition of Ni_2GaAs into NiGa and NiAs, suggesting that Ni_2GaAs is a metastable phase [1]. Both Oelhafen et al. [3] and Kuan [4] have reported the formation of Pd_2GaAs phases after annealing at 250° C. Earlier investigators [5,6] claimed to have observed PdGa after annealing at this temperature and a combination of PdGa, Pd_2Ga and $PdAs_2$ after annealing at 350°C.

Because of the potential importance of ternary phases as contact materials, we have investigated the Pd-GaAs system in order to identify the compounds formed during low temperature annealing and to resolve some of the discrepencies in previous studies. In this letter, the results of a transmission electron microscopy (TEM) study of the Pd-GaAs reaction are described. It is shown that the first two reaction products are phases of the type Pd_xGaAs. A detailed description of the morphological development

of the Pd-Ga-As reacted layer is given in reference 7.

EXPERIMENTAL METHODS

Gallium arsenide substrates with (100) orientation were prepared for metal deposition by immersion into a 9:1 DI H_2O:HCl solution for 10 sec. followed by a DI H_2O rinse. The GaAs surface was blown dry with N_2. Palladium was then deposited by electron beam evaporation to a thickness of 50 nm at a rate of 0.6 nm/s in a vacuum of 1-2 x 10^{-6} torr. Annealing treatments were performed in flowing forming gas (95% Ar and 5% H_2) for 10 min. at temperatures between 220 and 480°C.

Cross-sectional TEM (XTEM) specimens were prepared by argon ion milling with a liquid nitrogen cooled stage. Plan-view and XTEM specimens were observed in a Siemens 102 TEM operated at 100 keV and a JEOL JEM 200 CX with an ultra-high resolution pole piece operated at 200 keV, respectively. Energy dispersive spectrometry (EDS) of x-rays was performed with a Kevex model 3400 ultra-thin-window detector and System 8000 spectrometer mounted on a JEOL 200 CX TEM/STEM. A GaAs standard was used for partial quantification of the EDS spectra. Since a reliable Pd-Ga standard was not available, the [Pd]:[Ga] ratios reported below must be considered tentative.

RESULTS AND DISCUSSION

The plan-view micrograph and diffraction pattern in Fig. 1 (a,b) reveal that the first phase formed during low temperature annealing is nearly monocrystalline and has a well-defined orientation relationship with the GaAs substrate. Cross-sectional images from these samples (e.g. Fig. 2(a)) show that phase I is hexagonal with

$$a_o = 0.673 \pm 0.002 \text{ nm}$$

and

$$c_0 = 0.338 \pm 0.001 \text{ nm}.$$

The orientation relationship with (100) GaAs is

$$[0001]_I \; // \; [011]_{GaAs}$$

and

$$(2\bar{1}\bar{1}0)_I \; // \; (100)_{GaAs}.$$

Analysis of EDS data suggests a nominal composition of $Pd_5(GaAs)_2$ for phase I. These results are in close agreement with the findings of Kuan [4].

Phase I is the dominant reaction product in the as-deposited state and after annealing at temperatures up to 315° C [7]. During annealing at temperatures between 250 and 400° C, a second phase is formed if the initial Pd thickness is greater than ∿20 nm. This second phase appears to nucleate at fast diffusion paths such as grain boundaries, pores or cracks in the phase I film. The resulting morphology is shown in Fig. 1(c). At higher temperatures (eg. 350 and 410°C) phase II is the dominant phase in direct contact with GaAs. Figure 2(b) is a cross-sectional image of the phase II/GaAs interface after annealing at 350° C. The inset diffraction pattern along with diffraction patterns from plan-view samples confirm that phase II is also hexagonal with

$$a_0 = 0.92 \pm 0.01 \text{ nm}$$

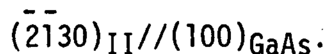
and

$$c_0 = 0.370 \pm 0.005 \text{ nm}.$$

In samples annealed below 400°C, phase II exhibits the following orientation relationship with (100) GaAs:

$$[0001]_{II} // [011]_{GaAs}$$

and



$$(\bar{2}\bar{1}30)_{II}//(100)_{GaAs}.$$

This orientation relationship is evident in Fig. 2(b). Adjacent grains of phase II are often observed to be in twin orientation with $[100]_{GaAs}$ parallel to either $[\bar{2}\bar{1}30]_{II}$ or $[\bar{1}\bar{2}30]_{II}$. Analysis of EDS spectra from grains of phase II yields a nominal composition of Pd_4GaAs.

In addition to phases I and II, Pd_2Ga was detected by XTEM for some annealing conditions [7]. However, a previously reported phase, $PdAs_2$ [5,6], has not been detected in any of our samples. Furthermore, under annealing conditions (250 C < T < 500° C) similar to those which yielded $PdAs_2$ as a major phase in previous studies [5,6], our samples contained hexagonal Pd_4GaAs as the major phase. Since previous identifications of $PdAs_2$ were based on x-ray diffraction data only, we have compared the published experimental diffraction spectra from samples said to contain $PdAs_2$ [5,6] with the calculated peak positions for phase II ($\sim Pd_4GaAs$). Table 1 shows that the peaks attributed solely to $PdAs_2$ can also be attributed to the ternary phase, Pd_4GaAs.

CONCLUSION

It is clear from these results that the Pd-GaAs reaction at low temperatures (< 500 °C) is dominated by the formation of ternary phases. If the lateral inhomogeneities can be limited by proper choices of the initial Pd layer thickness and the reaction temperature, these ternary phases may find application as shallow contact materials in direct analogy to the application of silicides as shallow contacts to silicon. In addition, since the reactions to form M_xGaAs phases do not involve the interfacial accumulation of arsenic, studies of the electrical properties of $M_xGaAs/GaAs$

interfaces should provide new insight into the factors which determine the barrier heights of metallic phases on n and p type GaAs.

ACKNOWLEDGEMENTS

The authors would like to thank the staff of the National Center for Electron Microscopy, Lawrence Berkeley Laboratory and Ariel Dori of Bell Laboratories, for technical assistance. One of the authors (T.S.) wishes to acknowledge Dr. T.R. Dinger and C. Echer for assistance with the EDS analyses, and Ms. G. King for aiding in the preparation of TEM specimens. Many valuable discussions with Professor M-A. Nicolet of the California Institute of Technology are also gratefully acknowledged.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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TABLE 1

Comparison of diffraction peak positions for $PdAs_2$ and phase II*

Approximate peak position (2θ) measured from Fig. 1 of [5]	indexing based on $PdAs_2$[5]	calculated 2θ for $PdAs_2$	possible indexing as phase II	calculated 2θ for phase II
26.6 ± 0.2	111	25.8	$0\bar{1}11$	26.6
30.8 ± 0.2	200	29.9	$2\bar{1}\bar{1}1$	31.0
33.5 ± 0.2	212	45.5	$0\bar{2}21$	33.0
+36.5 ± 0.2	211	36.8	--	--
50.7 ± 0.2	311	50.6	$0\bar{1}12$	50.7
70.0 ± 0.2	420	70.4	$0\bar{4}42$	69.4
‡72.3 ± 0.2	421	72.4	--	--
73.9 ± 0.2	332	74.4	$2\bar{7}50$	74.5

* assuming CuKα radiation (λ = 0.1542nm) and $a_0[PdAs_2]$ = 0.5982nm.

+ peak overlaps with 200 PdGa

‡ peak overlaps with 321 PdGa

FIGURE CAPTIONS

Fig.1 Low magnification TEM images and corresponding diffraction patterns from plan-view specimens of samples annealed for 10 min. at (a,b) 220°C and (c,d) 315°C. The diffraction pattern in (b) is the superposition of the polycrystalline Pd ring pattern and the monocrystalline phase I spot pattern in $\langle 2\bar{1}\bar{1}0 \rangle$ zone-axis orientation. Diffraction spots from phases I and II are visible in (d).

Fig.2 Cross-sectional TEM images of (a) the phase I/GaAs and (b) the phase II/GaAs interfaces. Samples were annealed at 275 and 350°C respectively. The images and their corresponding electron diffraction patterns illustrate the orientation relationships described in the text. Gallium arsenide is in $\langle 011 \rangle$ zone-axis orientation. Phases I and II are in $\langle 0001 \rangle$ zone-axis orientation.

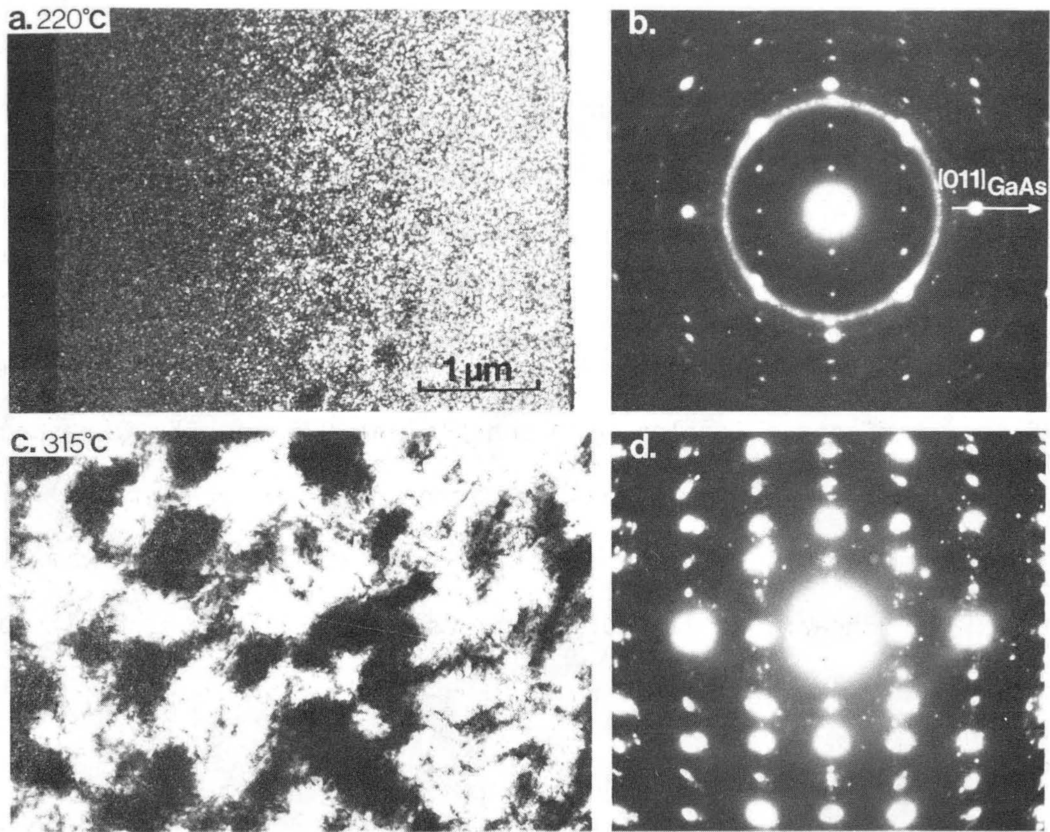

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Fig. 1

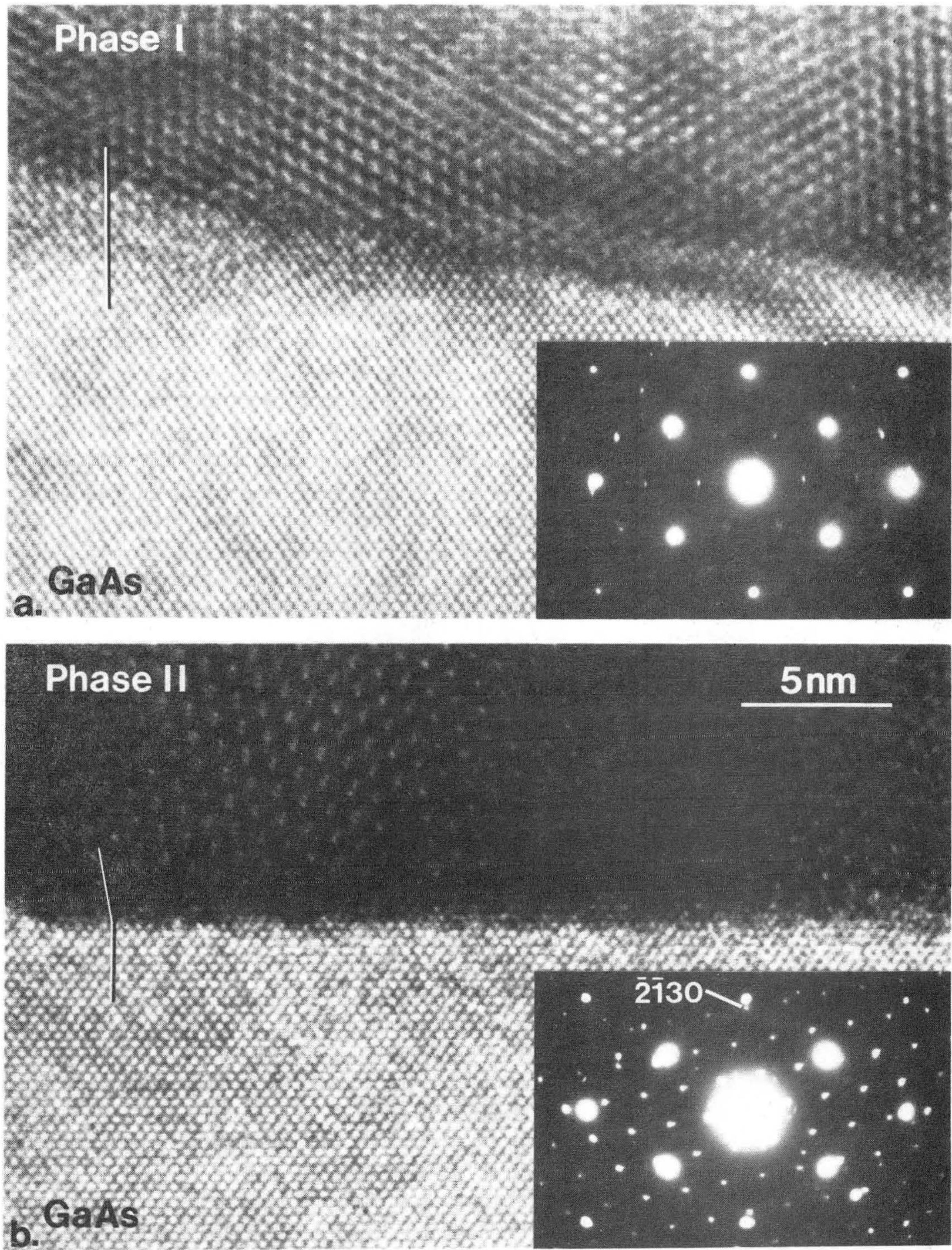

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Fig. 2

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