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Sands, T.

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T. Sands, V.G. Keramidas, J. Washburn,
and R. Gronsky

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On The Structure and Composition of Ni_xGaAs

T. Sands[a] and V.G. Keramidas
Bell Communications Research, Inc.,
600 Mountain Avenue,
Murray Hill, NJ 07974

J. Washburn and R. Gronsky
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory,
University of California,
Berkeley, CA 94720

Abstract

Advanced compound semiconductor devices require increasingly stable, shallow and uniform metallized layers for ohmic and Schottky contacts. However, the design of new multielemental contact metallization systems is limited by the paucity of information regarding the structure, composition and stability of phases resulting from the interaction of single metal layers with compound semiconductors. In this letter, the results of a transmission electron microscopy investigation of the Ni/GaAs reaction are presented. The first reaction product is shown to have the composition Ni_3GaAs. Based on this composition and lattice parameter measurements, it is proposed that the structure of Ni_3GaAs is closely related to that of $\gamma' Ni_3Ga_2$, a derivative of the hexagonal B8 structure type.

As stability and performance criteria for contacts to compound semiconductor devices become more stringent, the need to understand and control metal/semiconductor interface reactions and electrical

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[a] Work performed as a visiting Industrial Fellow at the Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

properties becomes more acute. The first step toward understanding the behavior of complex metallization systems is to investigate the interactions between single metal layers and compound semiconductor substrates. Of particular interest are the metals which react to form adherent ternary compound layers with composition M_xAB since these reactions do not involve the accumulation of anions at the contact/AB semiconductor interface.[1] Thus far, two metals, Ni[2-4] and Pd[1,5-7] have been found to react with GaAs at low temperatures (<300 °C) to form M_xGaAs phases. Detailed transmission electron microscopy (TEM) studies of the Pd/GaAs reaction have been reported by Sands et al[1,7] and Kuan et al.[6] Several studies of the Ni/GaAs system have been published,[2-4] however, as will be discussed below, there are discrepencies in the reported lattice parameters and composition of the first phase, Ni_xGaAs. In this letter, the nominal composition of the ternary phase is shown to be Ni_3GaAs. On the basis of this information a tentative structural model of Ni_3GaAs is proposed.

Gallium arsenide (100) substrates were prepared for Ni 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. Nickel was then deposited by e-gun evaporation to a thickness of 44nm at a rate of 1nm/sec in a vacuum of $1\text{-}2\times10^{-6}$torr. Annealing treatments were performed in flowing forming gas (95%Ar and 5%H_2). Cross-sectional TEM specimens were prepared by Ar

ion milling with a stage cooled by liquid nitrogen. Plan-view and cross-sectional TEM specimens were examined in a JEOL JEM 200 CX operated at 200 KeV. Energy dispersive spectrometry (EDS) of x-rays was performed with a Kevex high-angle detector and system 8000 spectrometer mounted on a JEOL 200 CX TEM/STEM.

From Fig. 1a it is apparent that Ni reacts with GaAs during deposition. Annealing at 220°C for 10 min. is sufficient to fully react approximately 90% of the film area. As a result of the barrier action of the native oxide/hydrocarbon layer, 10% of the film area remains unreacted in the form of disc-shaped patches of Ni. In agreement with previous studies,[3,4] the reacted film consists of domains in four twin orientations. Two of these variants are readily identifiable in the diffraction pattern of Fig. 2. The hexagonal unit cell of the reacted phase exhibits the orientation relationship, $\{0\bar{1}1\}_{GaAs} \parallel \{01\bar{1}2\}_{Ni_xGaAs}$ and $\langle 011\rangle_{GaAs} \parallel \langle 2\bar{1}\bar{1}0\rangle_{Ni_xGaAs}$, with (100) GaAs. This is nominally the orientation relationship reported previously[2-4] except that the angle between $\{0001\}_{Ni_xGaAs}$ and $\{111\}_{GaAs}$ is $\sim 2°$. In other words, only the orientation relationship stated above is strictly observed. The measured lattice parameters of Ni_xGaAs are presented in Table I. Note that, unlike Lahav <u>et al</u>, we did not observe $c_o/a_o = \sqrt{3}/\sqrt{2}$ as would be required for a pseudocubic unit cell. This deviation from $c_o/a_o = \sqrt{3}/\sqrt{2}$ is reflected in the presence of vertical moire fringes in Fig. 2b. This interference pattern arises from the 3% misfit between the $\{01\bar{1}2\}$ and $\{2\bar{1}\bar{1}0\}$ planes of overlapping variants.

The compositions of the reacted layers after annealing at 220 °C and 315 °C were estimated by EDS from plan-view and cross-sectional samples. A typical EDS spectrum is presented in Fig. 3. Averaging over six spectra and using $k_{Ga/Ni} = 1.326$ where k is the proportionality factor relating the intergrated intensities of the K_α peaks to the weight percents of the elements, the ratio of [Ni] to the average of [Ga] and [As] was calculated to be 2.90 with a standard deviation of 0.24. Employing spectra from the GaAs substrate as standards, the [Ga] to [As] ratios were found to be 1.07 ± 0.01 and 1.28 ± 0.09 in the samples annealed at 220 and 315 °C, respectively. Thus, the nominal composition of the reacted layers after annealing at 220 and 315° C is Ni_3GaAs. The shift in [Ga]/[As] above ∿300° C probably results from the outdiffusion and evaporation of As.

Further confirmation of the Ni_3GaAs composition was obtained by cross-sectional TEM measurements of layer thicknesses using lattice images of the adjacent GaAs substrate for calibration. The film thickness was found to increase by a factor of 2.0 ± 0.1 as a result of the reaction. Given the measured unit cell volume, the unit cell should contain 3.0 ± 0.2 Ni atoms. Unreacted patches of Ni adjacent to fully reacted regions allowed estimation of the thickness of GaAs consumed by the reaction. The result of 57 ± 2 nm of GaAs consumed to create 88 ± 2 nm of Ni_xGaAs gives $x = 3.2 \pm 0.4$ and $[Ga] \cong [As] = 1.44 (\pm 0.08) \times 10^{22}$ atoms/cm^3. Again, these calculations suggest a nominal composition of Ni_3GaAs. It is interesting that Ogawa[2] reported that 110 nm of Ni reacted

to form 230 nm of Ni_xGaAs, consuming 150 nm of GaAs in the process. These measurements indicate a composition of Ni_3GaAs yet his Auger electron spectroscopy (AES) data suggested Ni_2GaAs. Lahav et al[3] also calculated a composition of Ni_2GaAs based on AES measurements. Whether this discrepency is due to truely different compositions or instead is a result of systematic errors in AES quantitation remains to be determined.

Knowledge of the composition and unit cell dimensions allows speculation as to the atom positions in the Ni_3GaAs unit cell. Since phases in both the Ni-Ga and Ni-As binary systems adopt the B8 structure with lattice parameters similar to those measured for Ni_3GaAs (see Table 1), it is reasonable to propose that Ni_3GaAs is also based on the B8 structure. Compositionally, Ni_3GaAs is most similar to γ' Ni_3Ga_2 which is derived from a "half-filled" B8 structure.[8] Thus we suggest a tentative structure for Ni_3GaAs constructed by the substitution of As for approximately one half of the Ga atoms in Ni_3Ga_2. In this model, the (0,0,0) and (0,0,1/2) positions are occupied by Ni atoms, the (1/3,2/3,3/4) and (2/3,1/3,1/4) positions are occupied by one Ni atom and a vacancy, and the (1/3,2/3,1/4) and (2/3,1/3,3/4) positions are occupied by one Ga and one As atom. Ordering of Ni vacancies probably results in the $2a_0 \times c_0$ and $3a_0 \times c_0$ superstructures that we observe in the samples annealed at 315°C. Previous investigators[2,4] have also observed superlattice spots after annealing at 300°C.

Hypothetically, the B8 structure can accommodate $x = 2$ (both (1/3,2/3,3/4) and (2/3,1/3,1/4) sites unoccupied) to $x = 4$ (both

sides occupied by Ni). Consequently, the homogeneity range of Ni_xGaAs may be quite broad. The observation that high temperature (>400° C) annealing leads to the formation of NiGa and NiAs[2,3] indicates that Ni_3GaAs is not a stable phase in the presence of excess GaAs. In other words, the formation of the binary phases from Ni_3GaAs involves the further consumption of GaAs. Of course, this observation does not preclude the possibility that Ni_3GaAs is a stable phase in the Ni-Ga-As system. From a practical standpoint, determination of the structure and composition of Ni_xGaAs allows accurate predictions of the amount of GaAs consumed during annealing of a shallow contact employing Ni. However, the apparent instability of Ni_3GaAs in the presence of GaAs would seem to limit the application of Ni_3GaAs as a contact material to GaAs.

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TABLE 1. Lattice Parameters of Ni_xGaAs

Annealing T(°C)	Phase	a_o[nm]	c_o[nm]	c_o/a_o	$d_{01\bar{1}2}/d_{\bar{2}\bar{1}10}$
220[a]	Ni_3GaAs	0.390±0.001	0.501±0.002	1.285±0.005	1.032±0.004
315[a]	Ni_3GaAs	0.388±0.001	0.507±0.002	1.305±0.005	1.043±0.004
410[a]	Ni_3GaAs	0.379±0.001	0.501±0.002	1.322±0.005	1.051+0.004
300[b]	Ni_2GaAs	0.384	0.496	1.292	1.035
300[c]	Ni_2GaAs	0.3925	0.4807	$1.2248=\sqrt{3}/\sqrt{2}$	1.000
	NiAs[d]	0.362	0.503	1.39	1.084
	$Ni_{.64}Ga_{.36}$[e]	0.400	0.498	1.25	1.011

[a] This study

[b] Reported by Ogawa[2] for Ni_2GaAs on (111)A GaAs.

[c] Reported by Lahav *et al*[3] for Ni_2GaAs on (100) GaAs

[d] R.D. Heyding and L.D. Calvert, Can. J. Chem. 35, 1205 (1957).

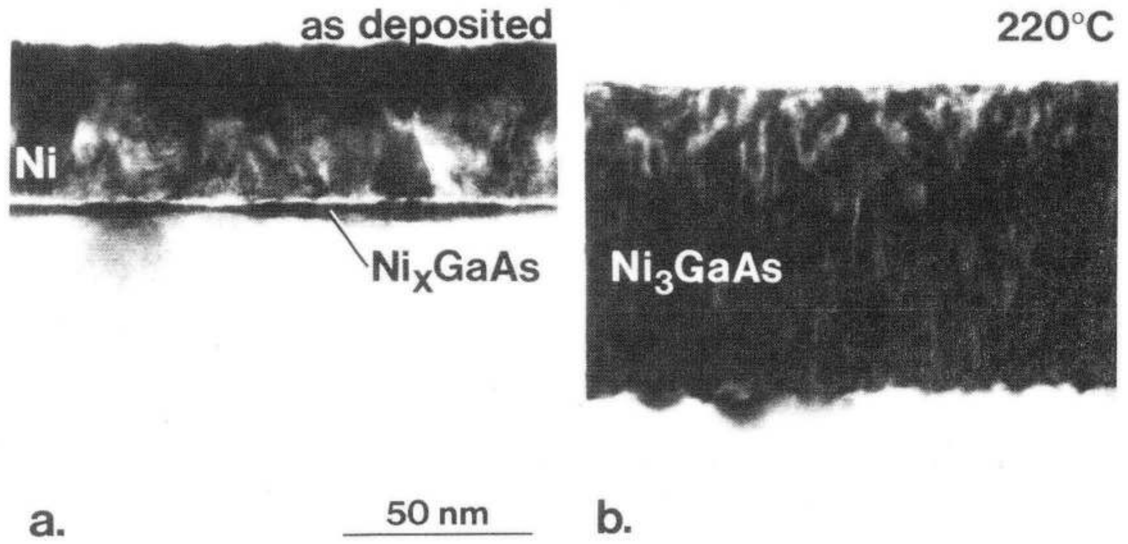
[e] See reference [8].

Figure Captions

FIG. 1. Cross-sectional TEM images of a) as-deposited Ni/GaAs and b) after annealing at 220 ° C for 10 min. Native oxide/hyrdocarbon layer appears as light band in a. Note that Ni_xGaAs is formed during deposition. Note the strain contrast at the interface in b).

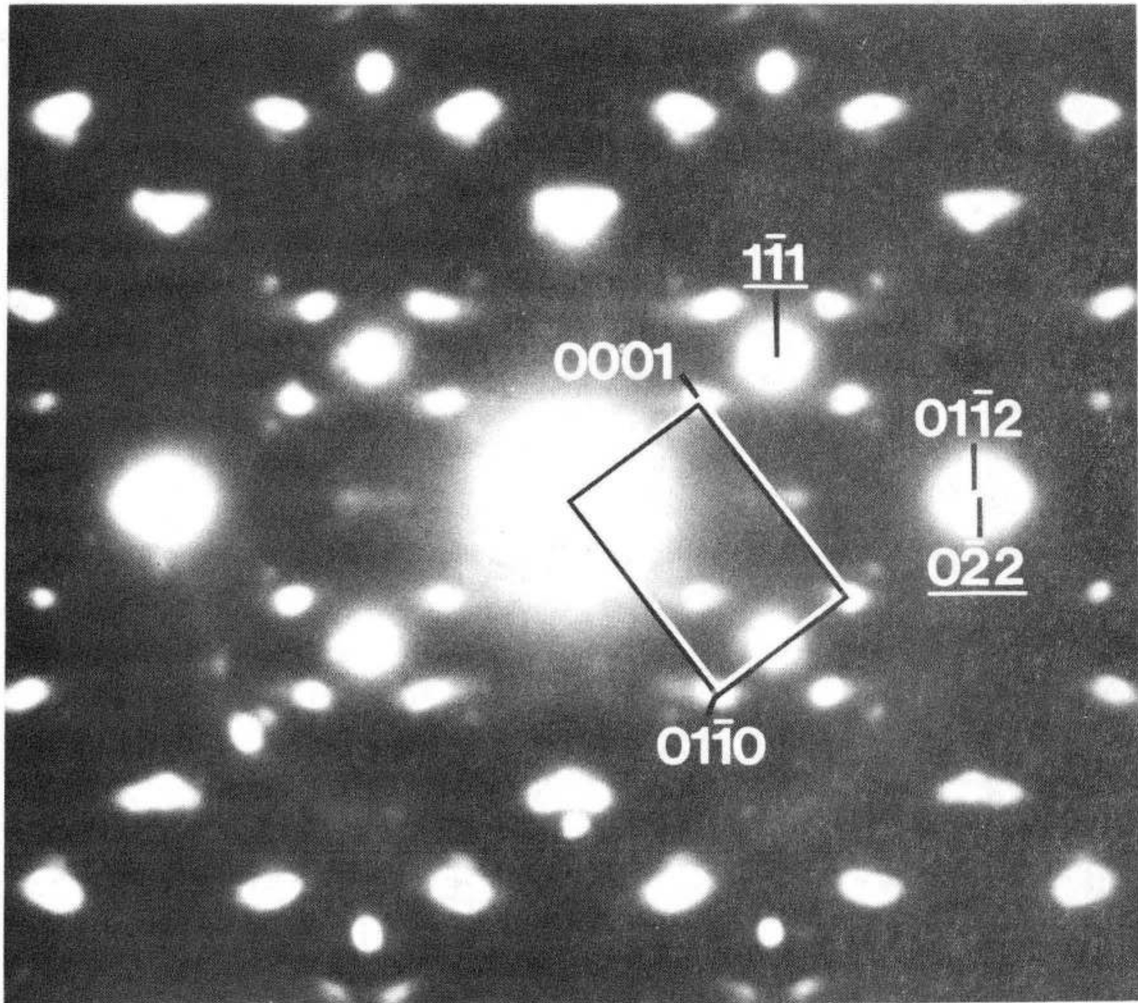
FIG. 2. Diffraction pattern from cross-sectional TEM specimen annealed at 315°C for 10 min. Two variants of Ni_3GaAs in $\langle 2\bar{1}\bar{1}0 \rangle$ zone-axis orientation are readily distinguishable. Diffraction pattern from one variant is outlined. Underlined indices indicate GaAs reflections. GaAs is in <011> zone-axis orientation.

FIG. 3. Energy dispersive x-ray spectrum from plan-view sample after annealing at 315° C for 10 min. Nominal film composition is Ni_3GaAs.



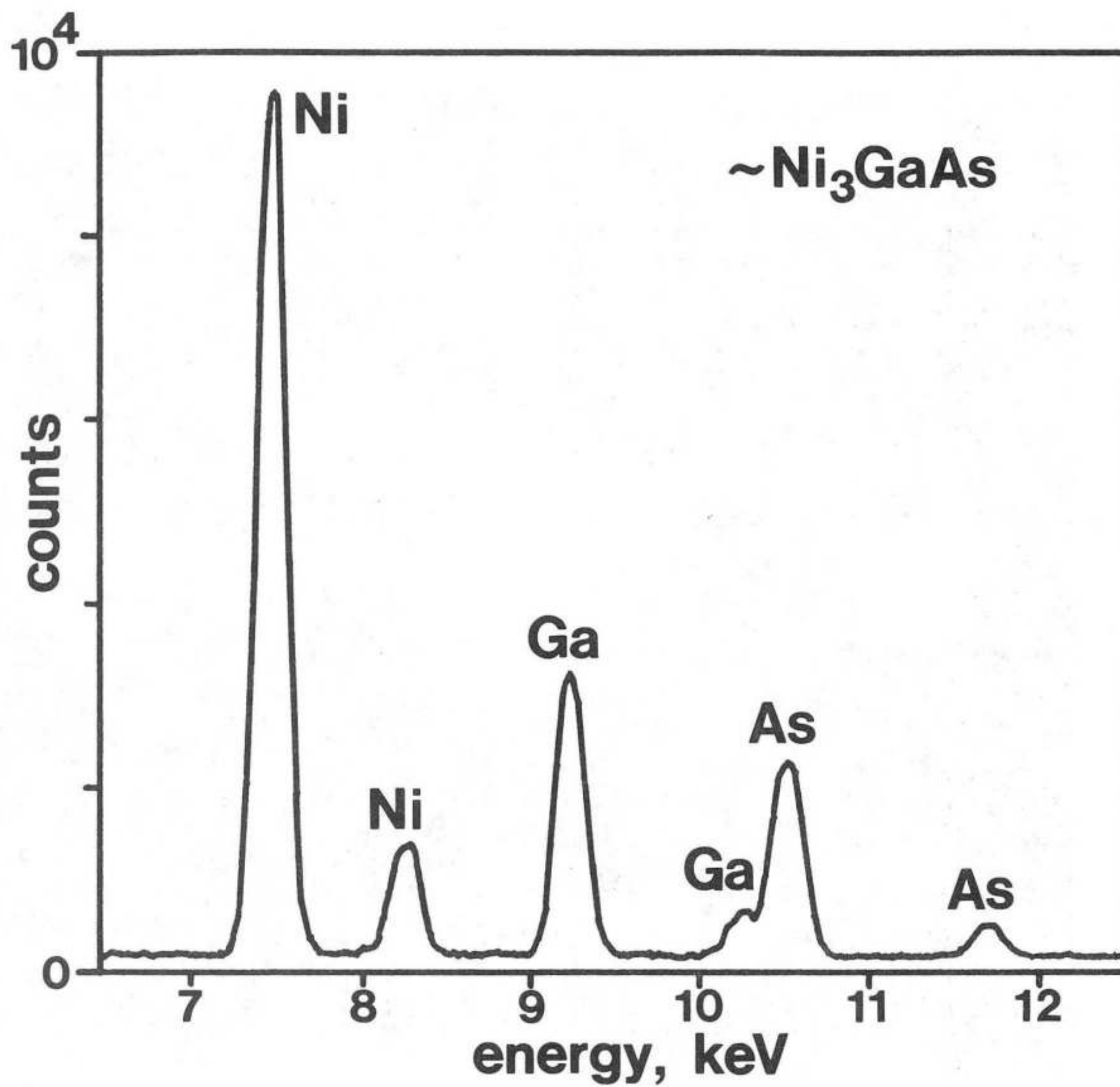
XBB 857-5850A

Fig. 1



XBB 858-6330

Fig. 2



XBL 858-3750

Fig. 3

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TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720