METALLURGICAL AND ELECTRICAL PROPERTIES OF ALLOYED Ni/Au–Ge FILMS ON $n$-TYPE GaAs

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Abstract—An experimental study of the alloying characteristics of a composite thin-film structure which is often used as an ohmic contact to GaAs is presented. A Au–Ge layer of eutectic composition covered by a thin-film of Ni and deposited on $n$-type epitaxial GaAs is investigated in order to better understand the relationship between the alloying behavior and the electrical properties of the contact. The barrier energy $\varphi_m$, and the specific contact resistance of the Ni/Au–Ge/GaAs system is measured for a wide range of alloy temperatures and times. The metallurgical properties of the Ni/Au–Ge/GaAs system are obtained with Auger electron spectroscopy and scanning electron microscopy. Auger spectroscopy combined with in situ sputter etching is used to determine depth-composition profiles for all constituents of both as-deposited and alloyed Ni/Au–Ge/GaAs contacts. In samples heat-treated below the Au–Ge eutectic temperature, Ni is found to move rapidly through the intervening Au–Ge layer to collect at the GaAs interface, and the effective value of $\varphi_m$ rises to the value characteristic of Ni/GaAs Schottky diodes. For heat-treatment above the Au–Ge eutectic temperature, ohmic contact behavior is observed, and uniform alloyed contact surfaces are found to result from the presence of Ni at the GaAs interface. Ga outdiffusion and surface accumulation resulting from GaAs dissociation occurs for all alloy temperatures and times. The Ga outdiffusion appears to be characterized by a very low activation energy.

\[ \Delta \varphi \] amount the contact barrier energy is lowered by non-zero electric field (eV)
\[ \rho \] resistivity of GaAs epitaxial layer (\( \Omega \) cm)

NOTATION

- $A$ contact area (cm$^2$)
- $A^{**}$ effective Richardson constant for metal–semiconductor interface, (A cm$^{-2}$ K$^{-2}$)
- $a$ length of side of square contact (cm)
- $C$ depletion capacitance of metal–semiconductor contact (F)
- $D$ diffusion constant for Ga (cm$^2$ sec$^{-1}$)
- $D_0$ constant used to describe temperature dependence of $D$ (cm$^2$ sec$^{-1}$)
- $E$ electron energy (eV)
- $E_a$ activation energy for Ga diffusion (eV)
- $h$ thickness of epitaxial GaAs layer (cm)
- $I_F$ forward current (A)
- $J_F$ forward current density (A cm$^{-2}$)
- $k$ Boltzmann’s constant (J K$^{-1}$)
- $N(E)$ number of secondary electrons of energy $E$
- $N_D$ net donor density in GaAs near the metal–semiconductor interface (cm$^{-3}$)
- $q$ electronic charge (C)
- $R_b$ resistance of the GaAs substrate and back contact (\( \Omega \))
- $R_T$ total resistance of sample (\( \Omega \))
- $r_c$ specific contact resistance (\( \Omega \) cm$^2$)
- $T$ absolute temperature (K)
- $T_a$ alloying temperature (K)
- $t$ total sputtering time (sec)
- $t_a$ alloying time (sec)
- $V_F$ forward voltage (V)
- $V_n$ difference between lower conduction band edge and Fermi level (eV)
- $V_R$ reverse voltage (V)
- $x_0$ thickness of Ni/Au–Ge film (cm)
- $\varepsilon$ permittivity of GaAs (F cm$^{-1}$)
- $\varphi_m$ potential barrier at interface of metal and $n$-type GaAs (eV)

1. INTRODUCTION

Solid-state devices using GaAs and compound semiconductors similar to GaAs are finding increasingly wider device applications as field-effect transistors, Gunn-effect diodes, IMPATT diodes and light-emitting diodes. For all of these devices, high efficiency and high reliability depend on low resistance ohmic behavior at one or more contacts. However, the lack of a reproducible and reliable ohmic contact to moderately doped $n$-type GaAs has been a persistent problem in metal–semiconductor technology. A simple and thus widely used technique to overcome this problem is to alloy suitable evaporated metal layers, such as Ni–Au–Ge, to clean GaAs in order to obtain a low resistance ohmic contact. We report here a detailed electrical and metallurgical study of the Ni/Au–Ge contact system on epitaxial GaAs; unique to our study is the use of a new thin-film profiling technique which employs Auger electron spectroscopy and sputter etching. Our results demonstrate GaAs decomposition and Ni, Au, and Ge interdiffusion occur during alloying. Furthermore, the spatial distributions of the constituents of the Ni/Au–Ge/GaAs system are related to the observed electrical properties. This work is an extension of the
preliminary metallurgical study reported earlier on bulk material only[1].

Several multilayer, alloyed thin-film systems have been developed as ohmic contacts to n-type GaAs[2-4]. A system consisting of a Au–Ge film of eutectic composition covered by a Ni film was first introduced by Braslau, et al. for making ohmic contacts to Gunn-effect devices[2]. It was found that when the contact was heat-treated above the Au–Ge eutectic temperature (360°C), an ohmic contact was formed to n-type GaAs for a wide range of GaAs resistivity. During alloying the Ge apparently formed an n+ layer[5], sufficiently heavily doped to produce a linear current–voltage characteristic as a result of field emission at the contact interface. The Au provided a low eutectic temperature and was compatible with existing microelectronic processing and packaging techniques. It was found that the Au–Ge alone did not wet the GaAs surface well during alloying but the presence of a small amount of Ni (2-11% wt) greatly improved surface uniformity of the alloyed Au–Ge contact. Braslau, et al. proposed that the Ni film did not melt during heat treatment, and thus provided a cover to hold the liquid Au–Ge in uniform contact with the GaAs surface[2]. Later measurements have shown the contact resistance for the Ni/Au–Ge system on n-type GaAs of 10^5 cm^-3 impurity concentration to be approximately 10^7 to 10^2 Ω-cm[7,8]; other alloy contacts used on n-type GaAs have produced similar contact resistance values[3-4].

The primary objective of this study was to examine the metallurgy of Ni/Au–Ge/GaAs contact formation using Auger electron spectroscopy and to correlate the metallurgical behavior with the electrical properties of the contact. Auger spectroscopy combined with in situ sputter etching has already been shown to yield valuable information about the interdiffusion, the segregation, and the distribution of the elements of a wide variety of other thin-film structures[9-11]. The depth-composition profiles obtained using this technique are shown in this study to reveal information about the Ni/Au–Ge/GaAs system not previously available by other analysis techniques. Rutherford backscattering of He ions were used by Gyulai, et al.[12] for an extensive study of both Au/GaAs and Au–Ge/GaAs contacts; their results revealed a damaged layer exists at the contact interface but the distribution of Ge in the alloyed region could not be determined. Harris, et al.[13] has used reverse-bias Schottky-barrier capacitance to study the Ni/Au–Ge/GaAs system; their results were limited by the lack of adequate in-depth spatial resolution. By comparison, Auger electron spectroscopy offers an in-depth spatial resolution (typically 10 Å) that is vastly superior to either that obtainable with Rutherford scattering or differential capacitance measurements. Furthermore, unlike Rutherford scattering, Auger spectroscopy can detect all of the elements of the Ni/Au–Ge/GaAs system with about equal sensitivity. In this work we have applied Auger electron spectroscopy and sputter etching to characterize the Ni/Au–Ge contact on epitaxial GaAs in order to obtain a more complete fundamental understanding of the contact formation process. In particular, we have studied in detail two phenomena not previously reported: the movement of Ni and the decomposition of GaAs during contact formation.

2. SAMPLE PREPARATION

Samples were fabricated from vapor-grown (100) epitaxial GaAs wafers with a 10 μm epitaxial n-type film of 2.5 × 10^15 cm^-3 doping on a Te doped n+ substrate. The epitaxial layer was covered with 3000 Å of chemically vapor-deposited SiO_2 and the n+ backside was entirely covered with an alloyed Au–Ge ohmic contact. Each sample consisted of nine contact regions varying in area from 2.3 × 10^-4 to 1.6 × 10^-3 cm^2 in order to provide for electrical evaluation. The contact regions were selectively etched in the SiO_2 using conventional photolithography. In a subsequent etching step, approximately 4000 Å of GaAs, which may have been affected by the oxide deposit[14], was removed from the exposed contact regions. This was followed immediately by the vacuum deposition of an Au–Ge film of typically 400 Å thickness from a preform of eutectic composition (88% Au–12% Ge by weight). A Ni film of about 150 Å thickness was separately deposited over the Au–Ge layer in the same vacuum. Metal contact regions were defined by selective etching using photolithography and the wafers were then separated into individual samples. Heat treatment of each sample was accomplished in a flowing N_2 atm. in an open-tube furnace with a characteristic thermal time constant of less than 40 sec.

3. ELECTRICAL EVALUATION

Electrical characterization of each sample was performed both before and after alloying by measuring the metal–semiconductor barrier energy φ_AE (eV) and the specific contact resistance r_s (Ω-cm^2). The barrier energy is most often used to characterize a rectifying contact while the specific contact resistance is a convenient parameter for describing an ohmic contact. If φ_AE is large and if the doping concentration in the semiconductor is low, current flow across the interface will be controlled by thermionic emission; the resulting r_s will be very large. However, if the doping concentration is high, the depletion width will be small and electrons can tunnel through the potential barrier (i.e., field emission); the resulting r_s will be small. Thus, data on φ_AE and r_s reveal information about the nature of the electron transport.

*Samples have also been fabricated by the separate deposition of Au, Ge and Ni layers, and similar results were obtained.
across the metal–semiconductor interface. Furthermore, the experimentally measured values of \( \varphi_{bn} \) and \( r_c \) can be used to estimate the net doping concentration at the metal–semiconductor interface and thus reveal whether during the alloying process a dopant was introduced into the semiconductor. Since the dopant may penetrate to only a small depth, its exact distribution and amount is often difficult to measure directly [12, 13].

Two different measurements were used to determine \( \varphi_{bn} \): from the forward-biased current–voltage characteristic the extrapolated saturation current was measured and related to \( \varphi_{bn} \) using thermionic emission theory, and from the depletion capacitance–voltage characteristic the extrapolated value of voltage for zero capacitance was measured and related to \( \varphi_{bn} \). If current flow across the metal–GaAs interface is primarily by thermionic emission of majority carriers over the barrier, then [15]

\[
J_F = A^{**} T^2 \exp \left( -\frac{q \varphi_{bn}}{kT} \right) \exp \left( \frac{qV_F}{nkT} \right)
\]

where \( A^{**} \) is the effective Richardson constant for \( n \)-type GaAs \((8 \cdot 16 \text{ A/cm}^2 \cdot \text{K}^2)\), \( n \) is a factor to allow for deviation from theory, and \( J_F \) is the current density for a forward applied voltage \( V_F > 3kT/q \). By fitting equation (1) to \( I_F - V_F \) data such as shown in Fig. 1, both \( \varphi_{bn} \) and \( n \)

were determined for Ni/Au-Ge/GaAs samples heat treated below about 360°C. Samples heat treated above 360°C had \( n \)-values exceeding 1·20 which indicated equation (1) and thus thermionic emission did not accurately describe the contact \( I_F - V_F \) characteristic. The barrier energy was also determined by measuring the depletion capacitance \( C \) as a function of reverse voltage \( V_R \) and fitting the resultant data to [15]

\[
\frac{1}{C^2} = \frac{2A^2(\varphi_{bn} + \Delta \varphi) - V_N + V_R - kT/q}{q\epsilon N_D}
\]

where \( \Delta \varphi \) is the barrier lowering energy, \( V_N \) is the energy difference between lower conduction band edge and the Fermi level, and \( N_D \) is the net donor density in the depletion region of the GaAs. Typical data are shown in Fig. 2 where \( \varphi_{bn} \) was found from the intercept on the voltage axis. The slight change in the slope for the alloyed sample compared to the as-deposited sample indicated a small decrease in \( N_D \) may have occurred during alloying near the metal–GaAs interface.

Figure 3 summarizes \( \varphi_{bn} \) data for Ni/Au-Ge/GaAs samples alloyed for 2 min at various temperatures. The as-deposited value of \( \varphi_{bn} = 0.68 \pm 0.06 \text{ eV} \) for the Ni/Au-Ge/GaAs system compares favorably with that reported by Pruniaux [8] for the Au-Ge/GaAs system. From Fig. 3 it is apparent that \( \varphi_{bn} \) increased by about 0·15 eV after heat-treatment for 2 min at just below the Au-Ge eutectic temperature. Other experiments indicated that as long as the alloy temperatures remained below about 360°C, \( \varphi_{bn} \) would eventually rise to a constant value of 0·83 ± 0·05 eV. Above 360°C, a significant drop in \( \varphi_{bn} \)
was found (Fig. 3) but accurate values of $\varphi_{\text{as}}$ could not be obtained as the Ni/Au–Ge/GaAs system became increasingly ohmic.

Because the total sample resistance varied over an extremely wide range, the specific contact resistance $r_c$ was measured by two different means. For rectifying samples with $r_c > 10^{-2} \, \Omega \cdot \text{cm}^2$, $r_c$ was determined from $I$–$V$ data measured below 5 mV applied bias. For near ohmic samples with $r_c < 10^{-2} \, \Omega \cdot \text{cm}^2$, the spreading resistance of the thin epitaxial layer and the residual sample resistance had to be carefully separated from the Ni/Au–Ge/GaAs contact resistance. The technique of Cox and Stack [3] was used to accomplish this separation by measuring the dependence of total resistance on contact area and comparing the results to the following equation:

$$ R_T = \frac{r_c}{a^2} + \sqrt{\left(\frac{\pi}{4}\right) \frac{\rho}{\pi a} \arctan \left(4 \sqrt{\left(\frac{\pi}{4}\right) \frac{h}{a}}\right)} + R_0 $$

(3)

where $R_T$ is total resistance of a square contact of side $a$ in length, $\rho$ is the resistivity of the epitaxial layer of thickness $h$, and $R_0$ is the resistance of the back contact and $n^+$ substrate. Equation (3) above is a slightly modified form of equation (5) of Cox and Stack [3] which describes the total resistance of a circular contact rather than a square contact. The form of the second term, which represents the spreading resistance, has been assumed to be unaltered by the change in geometry since the spreading resistance is only weakly dependent on the exact contact shape [16]. The factor $\sqrt{\pi/4}$ arose from setting the area of the square contact equal to that of the circular contact. Figure 4 shows typical $R_T$ vs $1/a$ data for a sample alloyed above 360°C. The scatter in the data allowed determination of $r_c$ to within only ±25 per cent; however, this degree of accuracy was sufficient to indicate the relative quality of the contacts.

Figure 5 summarizes $r_c$ data for samples heat treated up to 800°C. The increase in $r_c$ from the as-deposited value to that for heat-treatment just below 360°C can be fully accounted for by the corresponding increase in $\varphi_{\text{as}}$, of Fig. 3 using thermionic emission theory and assuming a constant doping density at the metal–GaAs interface. Above the melting point of the Au–Ge film, $r_c$ drops to a minimum value at about 600°C for the 2 min alloy cycle. This drastic decrease in $r_c$ represents a change in the metal–semiconductor behavior from a rectifying Schottky diode to a low resistance ohmic contact. The low values of $r_c$ observed in samples alloyed above 360°C is probably due to a substantial increase in net donor density at the metal–semiconductor interface since neither thermionic emission theory nor field emission theory predicts the significant decrease observed in $r_c$ if the net doping concentration is assumed to remain at original epitaxial-
determine the surface uniformity for alloyed samples as well as aid in interpreting the effect of sputter etching on the AES analysis. The results of the metallurgical evaluation were then correlated to the previously observed electrical behavior.

AES has been thoroughly reviewed in the literature[18, 19]; thus we present here only a brief description of AES as an introduction to our study. Basically, AES is a chemical analysis technique which consists of energy analyzing the electrons emitted from the surface of a sample bombarded by a kilovolt electron beam. The emitted electron energy spectrum contains peaks which are characteristic of the atoms on the surface undergoing bombardment. These characteristic peaks result from the ejection of Auger electrons which are produced during a relaxation process in the atoms ionized by the primary electron beam. The energy of an Auger electron is determined by atomic energy levels and thus uniquely identifies the parent atom. Furthermore, Auger electrons are created within a few monolayers of the surface since the mean escape depth has been measured to vary from only 3 to 30 Å[18]. Therefore, by using the readily available AES spectra for most of the elements[20], qualitative chemical analysis of solid surfaces can be easily performed. AES has now been extended to reveal the chemical states of the surface atoms[21] and to provide a quantitative estimate of monolayer surface coverage[22].

A schematic diagram of the energy analyzer used for AES in this work is shown in Fig. 6. The primary electron beam was produced by an electron gun mounted on the axis of a cylindrical mirror energy analyzer. Secondary electrons in a narrow energy range passed through the analyzer and were collected by the first dynode of the electron multiplier. The output from the analyzer was fed to a lock-in amplifier, and the entire energy spectrum was produced by sweeping the potential applied to a cylindrical electrode of the analyzer. The ion gun in Fig. 6 was used to clean the surface of the sample prior to AES analysis or for simultaneous ion sputtering and AES analysis. In all cases, AES analysis was carried out using a 3-keV 50-μA electron beam of about 100 μm dia. at the sample.

Figure 7 shows the system used to obtain both the AES spectrum and the depth-composition profile of the Ni/Au-Ge/GaAs contacts. A signal proportional to the energy distribution N(E) of the electrons entering the analyzer was fed to the lock-in amplifier. The differential distribution dN/dE was produced at the output of the lock-in amplifier by modulating the sweep voltage (proportional to energy E) and synchronously detecting with the lock-in amplifier. With the switch S in the Manual position, the AES spectrum* of the surface under examination was plotted on upper X-Y recorder. The

layer value. Using the field emission theory of Lepselter and Andrews[17], with the appropriate value of barrier energy indicated by Fig. 3 and the corresponding value of \( n_x \) from Fig. 5, the net impurity concentration at the interface for the sample heat treated at 600°C is estimated to be about \( 3 \times 10^{23} \) cm\(^{-3} \). Thus, in the samples studied here, the Ni/Au-Ge layer when alloyed above the Au-Ge eutectic temperature raised the doping concentration by over three orders of magnitude. The formation of an \( n \) layer then allows a large tunnel current to flow across the metal-GaAs interface with only a small voltage drop.

4. METALLURGICAL EVALUATION

Metallurgical analysis of the Ni/Au-Ge/GaAs thin-film system was accomplished with Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). AES analysis was used to identify the various elements present on the surface of samples before and after alloying. Furthermore, by combining AES with in situ sputter etching, depth-composition profiles for Ni, Au, Ge, Ga, and As were obtained for both alloyed and unalloyed samples. SEM examination was used to

*The differential spectrum dN/dE vs E, often called the AES spectrum, is recorded rather than N(E) itself since the Auger peaks are more readily identified in the dN/dE spectrum. By convention, the location of the minimum in the dN/dE spectrum is defined as the characteristic Auger energy.
location and shape of the Auger peaks were used to identify the element or elements on the surface of the sample. For quantitative analysis, the peak-to-peak amplitude $A$ for an Auger peak in the AES spectrum was assumed directly proportional to surface area covered by that element and unaffected by the presence of dissimilar elements on the surface[22].

With the switch $S$ of Fig. 7 in the Auto position, an in-depth profile for the sample being examined was automatically recorded. The multiplexer periodically sampled the peak-to-peak signal $A$ in a predetermined energy window while the specimen was slowly sputter etched. The output of the multiplexer was point-plotted on the lower $X$-$Y$ recorder as a function of sputtering
time $t$. If the sputtering rate remains constant, the $A-t$ plot must represent an in-depth composition profile of the sample. The amplitudes of up to six different Auger peaks could be recorded simultaneously. Typical sputtering rates were 5–15 Å/min, and the minimum detectable limit was observed to be approximately 0–05 atomic per cent under ideal conditions.

Typical depth-composition profiles for the Ni/Au–Ge/GaAs system for various alloy conditions are shown in Figs. 8–10. The peak-to-peak amplitude of an Auger peak, with characteristic Auger energy given in parentheses, for each constituent of the Ni/Au–Ge/GaAs system is plotted on a different vertical scale. To aid in comparing the distribution of one element with another, values for per cent surface coverage are given at convenient points in each figure. The per cent surface coverage for a given element was found by normalising to the signal level received from a clean surface covered only by the element in question. The per cent surface coverage obtained in this manner may differ from the true atomic percentage value since the effects of dissimilar species, variation of in backscattering coefficient, and variation in mean free path with Auger energy are not included in the normalisation procedure. The sputtering conditions for all three samples of Figs. 8–10 were identical: an Ar ion beam of 1 keV energy and 1 mm dia. at a pressure of $5 \times 10^{-5}$ torr.

The composition profile for the as-deposited sample of Fig. 8 shows a layered thin-film structure as expected. Note that although the Au and Ge were co-evaporated in a single step, the resulting film shows almost complete separation of the Ge and Au. A simple calculation of the relative evaporation rates [23] reveals that both the high mass and the large amount of Au present in the evaporation source will produce an Au-rich film at the GaAs surface. The ratio of the areas under the Ge and Au profiles of Fig. 8, taking into account the relative sputtering yields [24], agrees reasonably well with the volume ratio for a film of eutectic composition. Also shown in Fig. 8 is the distribution of the contaminant oxygen on an expanded vertical scale. The oxygen surface coverage was estimated by using an MgO sample as a standard. Besides indicating the degree of oxygen contamination during film deposition, the oxygen peaks locate two interfaces: at 10 min, the Ni interface and at 45 min, the GaAs interface. The oxygen peak at the GaAs interface may indicate the existence of a natural oxide on the GaAs surface prior to the Au–Ge deposit [25]. Note that Ni has apparently intermixed with the Ge either during the Ni deposition or subsequent processing.

Figure 9 is a typical profile for samples heat treated below the melting point of the Au–Ge eutectic. Ni has rapidly moved through the Au and Ge layers to accumulate near the original GaAs interface. The Ge also

![Fig. 8. Depth-composition profile for thin films of Ni (170 Å) and Au–Ge (410 Å) deposited on n/n+ (100) GaAs. Approximate per cent surface coverage values are indicated at critical points and energy values for the characteristic Auger peaks are given in parentheses. Typical as-measured data is shown for a portion of the Au distribution.](image-url)
Fig. 9. Depth-composition profile for the Ni/Au-Ge/GaAs system of Fig. 8 after heat treatment at 352°C for 2 min.

Fig. 10. Depth-composition profile for the Ni/Au-Ge/GaAs system of Fig. 8 after heat treatment at 503°C for 2 min.

shows similar behavior but to a lesser extent while the Au distribution remained relatively unchanged. Note the significant GaAs disassociation near the original GaAs interface, and the resulting Ga outdiffusion and accumulation on the surface of the sample. No evidence of a similar As outdiffusion has been found. The results on many samples heat treated below 360°C showed that the plateau in the As distribution near the original GaAs interface (at about 35 min in Fig. 9) occurred only when Ni had penetrated into that region. Although our results are
Fig. 11. SEM micrographs of sputter etched Ni/Au-Ge/GaAs samples alloyed at 470°C for 2 min. (a) Surface with about 26% Au remaining. (b) Surface with less than 2% Au remaining. The ion beam was incident from below, and the dark spot near the center of both micrographs is a defect in the SEM display.
Fig. 14. SEM micrographs of samples alloyed at 470°C for 2 min. (a) Au-Ge/GaAs sample. (b) Ni/Au-Ge/GaAs sample. The dark spot near the center of both micrographs is a defect in the SEM display.
incomplete as yet, Ni may be replacing Ga to form a nickel-arsenic compound in the vicinity of the original GaAs interface. Similar behavior has been reported for Pt/GaAs diodes which show evidence of PtAs$_x$ formation at the GaAs interface upon heat treatment[26, 27].

Ni/Au-Ge/GaAs samples alloyed at temperatures exceeding 360°C displayed depth-composition profiles similar to that of Fig. 10. A high Ga surface concentration was always observed prior to sputter etching, again indicating Ga outdiffusion and surface accumulation. However, the plot of Fig. 10 cannot be correctly interpreted as a depth-composition profile because SEM micrographs revealed that all samples alloyed above 360°C had non-uniform surfaces. The Ni/Au-Ge film balloted up on the GaAs surface during alloying, and thus the ion-milling process did not remove material in a uniform planar manner. Figure 11 illustrates the surface condition in alloyed samples which were sputter etched in the AES apparatus described above. Since the degree of agglomeration was severe and since the sputtering yield varies from element to element, preferential sputtering must have occurred during profiling. For example, the surface of Fig. 11(b) after extensive sputtering with an oblique-incidence ion beam shows evidence of shadows cast by the agglomerates. Without sufficient primary electron beam resolution, it was not possible to accurately identify the composition of the individual agglomerates by Auger spectroscopy. Therefore, data similar to Fig. 10 for samples heat treated above 360°C could not be directly interpreted as simple depth-composition profiles. However, samples heat treated below 360°C showed little or no evidence of agglomeration, and thus the data of Figs. 8 and 9 are believed to accurately represent depth-composition profiles.

The redistribution of Ni in the Ni/Au-Ge/GaAs system during alloying was measured as a function of alloy temperature and time. Figure 12 shows Ni composition profiles for various alloy temperatures with the alloy time fixed at 2 min. Below 360°C, the Ni distribution splits into two peaks; one located near the surface of the sample and one located near the GaAs interface. Figure 13 shows the variation of the amplitude of the two peaks with alloy time for a fixed temperature below 360°C. The Ni concentration at the GaAs substrate builds to about 50 per cent while the Ni concentration near the surface drops to below 15 per cent. For samples alloyed above 360°C, the Ni distribution could not be accurately obtained because of the non-uniform surface present after alloying.

The movement of the Ni to the GaAs surface is believed to be responsible for the change in the electrical properties observed in samples heat treated below the melting point of the Au-Ge film. In order to determine the electrical properties of the Ni/GaAs interface, Ni/GaAs samples were fabricated in the same manner and from the same GaAs material as the Ni/Au-Ge/GaAs samples. Both alloyed and the as-deposited Ni/GaAs samples had barrier energies of $\varphi_b = 0.83 \pm 0.02$ eV which agrees with the published value[28]. Note that from Fig. 3, this value

![Fig. 12. Depth-composition Ni profiles for Ni/Au-Ge/GaAs samples heat treated at different temperatures.](image-url)
of $\phi_{\text{eff}}$ also agrees with barrier energies measured in Ni/Au-Ge/GaAs samples heat treated at temperatures just below 360°C for 2 min. Thus, the movement of Ni to the GaAs interface raises the barrier energy and correspondingly increases the specific contact resistance of the Ni/Au-Ge/GaAs system when alloyed at temperatures below 360°C.

From the above data, it is evident that the role Ni plays in determining the surface uniformity of an alloyed Ni/Au-Ge/GaAs contact can now be better understood. Figure 14 shows SEM micrographs of Au-Ge and Ni/Au-Ge films on GaAs both alloyed above 360°C. Without the overlaying Ni film (Fig. 14(a)), the Au-Ge balls up and rectangular etch pits appear which are characteristic of the (100) GaAs surface [12]. With Ni present, however, the alloyed surface is much more uniform although not perfectly smooth on a sub-micron scale. From the AES profiles it is clear that the Ni does not remain on top of the Au-Ge layer but it moves rapidly under the Au-Ge layer before the Au-Ge melting point is reached. Thus the improvement in surface uniformity as a result of the inclusion of Ni is not that Ni acts as a blanket to hold the molten Au-Ge in uniform contact with the GaAs surface but rather the presence of Ni at the GaAs surface greatly improves the wetting of liquid Au-Ge to GaAs. This conclusion was supported by a separate experiment on samples fabricated with 100 Å Ni film placed between the Au-Ge layer and the clean GaAs substrate. These Au-Ge/Ni/GaAs samples showed essentially the same electrical and metallurgical properties as the Ni/Au-Ge/GaAs samples described above.

The Ga out-diffusion and surface accumulation was studied in detail and the results are summarized in Fig. 15. The Ga concentration as determined from AES data on the surface of unspattered samples is plotted as a function of the reciprocal alloy temperature. The scatter in the data may result from random variation in the degree of surface contamination. In order to compare the experimental results to simple diffusion theory, the solid line of Fig. 15 represents the function

$$\text{erfc} \left[ \frac{x_0}{2\sqrt{D_t}} \right]$$

where $x_0$ is total thickness of the Ni/Au-Ge film (assumed constant at 580 Å), $t_a$ is the alloy time fixed at 2 min, and $D$ is the diffusion constant for Ga in the composite Ni/Au-Ge layer with an assumed dependence on the alloy temperature $T_a$ of

$$D = D_0 \exp(-E_a/kT_a)$$

Fig. 15. Ga surface concentration for the Ni/Au-Ge/GaAs system as a function of alloy temperature at a fixed alloy time of 2 min. The solid line represents the theoretical behavior for a diffusion process described by a complementary error function and $E_a = 0.1$ eV.
where $D_0$ is a constant and $E_a$ is an activation energy. By fitting equations (4) and (5) to the Ga surface accumulation data, it is found that $D_0 = 2 \times 10^{-6}$ cm$^2$/sec and $E_a = 0.1$ eV. Since typical activation energies for bulk diffusion are from 1 to 2 eV, the low activation energy for Ga outdiffusion rules out bulk diffusion and indicates that diffusion through pinholes and cracks in the nonuniform alloyed Ni/Au-Ge layer is probably the dominant diffusion mechanism. Furthermore, the values of $E_a$ and $D_0$ found from Fig. 15 are supported by data found from separate measurements on samples heat treated at a constant temperature but for varying lengths of time. Although evidence as to the exact mechanism governing the Ga outdiffusion is yet at hand, it is clear that GaAs readily disassociates at relatively low temperatures and Ga rapidly diffuses through the overlying composite metal film to accumulate in large amounts on the surface. Recently, Ga outdiffusion and surface accumulation has been reported for Au/GaAs[27] and SiO$_2$/GaAs[14] structures.

5. SUMMARY AND CONCLUSIONS

The results of our study of the alloying behavior of the Ni/Au-Ge ohmic contact to epitaxial $n$-type GaAs can be summarized as follows:

(1) Heat-treatment below 360°C. The Au and Ge layers remain relatively unchanged from their as-deposited distributions while Ni moves rapidly through the intervening Au-Ge layer to collect at the GaAs interface. The presence of Ni at the GaAs interface increases $\varphi_m$, to that characteristic of a Ni/GaAs Schottky diode. The original GaAs surface dissociates and evidence of Ga outdiffusion and surface accumulation is found.

(2) Heat-treatment above 360°C. The Au-Ge melts and Ge enters the GaAs to apparently produce a heavily doped $n^+$ layer which results in ohmic electrical behavior. The presence of Ni at the GaAs interface greatly improves the wetting properties of the molten Au-Ge on GaAs and thus produces a relatively uniform contact surface after alloying. The Ga outdiffusion and surface accumulation increases significantly with increasing alloy temperature and time.

The observed GaAs dissociation may be responsible for the disordered region reported from Rutherford scattering data[12]. Furthermore, the Ga outdiffusion may affect how Ge dopes the GaAs material [2]. Ge is amorphous impurity in GaAs and whether it acts as a donor or acceptor in stoichiometric GaAs depends on the population of Ga vacancies relative to As vacancies. The large amount of Ga outdiffusion observed here without evidence of a similar outdiffusion of As may indicate a large number of Ga vacancies are present near the GaAs interface during alloying. Since Ge has been previously shown to act as a donor in GaAs when excess As exist [5], the Ga outdiffusion reported here may, in part, be responsible for the ohmic behavior of the alloyed Ni/Au-Ge/GaAs contact.

Finally, Gyulai, et al. have observed a deeply penetrating component of Au for alloyed Au and Au-Ge layers on GaAs using the Rutherford backscattering technique [12]. We have not observed a similar deep Au penetration for the Ni/Au-Ge/GaAs system using AES. Our results indicate an exponentially decreasing Au concentration which only penetrates into the GaAs epilayer to a depth less than the thickness of the as-deposited Au-Ge layer. Whether Ni is responsible for limiting the Au penetration in the Ni/Au-Ge/GaAs system is not known as yet.

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