Schottky barrier enhancement using reacted Ni_2Al_3/Ni/*n*-GaAs, Ni/Al/Ni/*n*-GaAs, and NiAl/Al/Ni/*n*-GaAs contacts

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(Received 27 April 1994; accepted for publication 11 January 1995)

A systematic study of the enhancement of Schottky barriers to *n*-GaAs has been carried out using the following diodes, Ni_2Al_3/*n*-GaAs, Ni_2Al_3/Ni/*n*-GaAs, Ni/Al/Ni/*n*-GaAs and NiAl/Al/Ni/*n*-GaAs, prepared by sputter deposition at a base pressure $\sim 2\times10^{-7}$ Torr. A high Schottky barrier height ranging from 0.95 to 0.98 eV (deduced from current-voltage measurements) was observed for all the annealed contacts except for Ni_2Al_3/*n*-GaAs. Enhancement of the Schottky barrier height in all the contacts was attributed to the formation of a high Al content (Al,Ga)As layer at the metal/semiconductor interface. A regrowth mechanism was used to rationalize the Schottky barrier enhancement. In this mechanism, Ni reacts with GaAs initially at low temperatures, forming Ni_xGaAs. The Ni_xGaAs layer then reacts with the Ni-Al layer on top to form the (Al, Ga)As layer under subsequent high temperature annealing. A (200) dark-field XTEM image of the annealed contact was used to demonstrate the existence of this (Al,Ga)As phase. © *1995 American Institute of Physics.*

I. INTRODUCTION

Schottky barrier height (SBH) to chemically prepared surfaces of *n*-GaAs is generally insensitive to the contact metals. However, attempts have been reported in the literature to enhance the Schottky barrier height to *n*-GaAs. A high SBH allows the fabrication of metal semiconductor field-effect transitors (MESFETs) with high switching efficiency and enhanced high-frequency switching performance.[1]

Several investigators[2-4] have used the following reacted contacts, $MoAl_{2.7}$/*n*-GaAs, NiAl/*n*-GaAs, and Ni/Al/Ni/*n*-GaAs, to enhance the SBH to near 1.0 eV. These high SBHs were attributed to the formation of a thin (Al,Ga)As layer at the metal/semiconductor interface. The mechanism leading to the formation of (Al,Ga)As was speculated to be an exchange reaction between Al and Ga at the interface. However, no convincing evidence was presented to support this exchange reaction. Our previous studies showed that the enhancement of SBHs for the annealed NiAl/*n*-GaAs contacts[5] was due to an exchange mechanism,[6,7] while that for the reacted Ni/Al/Ni/*n*-GaAs contacts[8] was due to a regrowth mechanism (RM).

The RM has been used by Sands *et al.*[9] to explain the formation of ohmic contacts to *n*-GaAs, but by Chen *et al.*[8] to rationalize the enhancement of the SBH of the Ni/Al/Ni/*n*-GaAs contacts. In this mechanism, Ni reacts with GaAs initially at low temperatures, forming Ni_xGaAs. The Ni_xGaAs layer is believed to react with the Ni-Al layer to form a (Al,Ga)As layer during a subsequent higher temperature annealing.

The objective of the present study are to

(i) make diodes of Ni_2Al_3/*n*-GaAs, Ni_2Al_3/Ni/*n*-GaAs, Ni/Al/Ni/*n*-GaAs and NiAl/Al/Ni/*n-GaAs using a sputter deposition technique,*
(ii) determine the Schottky barrier height of the above contacts as a function of annealing temperature using the current-voltage (*I*-*V*) method,
(iii) establish experimentally the existence of (Al,Ga)As at the interface, and
(iv) use the RM to rationalize the formation of (Al,Ga)As at the metal/semiconductor interface which is responsible for the enhancement of Schottky barrier height (ESBH).

II. EXPERIMENTAL METHODS

Unintentionally doped ($\sim 3\times10^{16}$ cm^{-3}) *n*-GaAs wafers with a (100) orientation were used as substrates in the present study. A standard photolithographic liftoff process was used for fabricating the contacts. The substrates were degreased with trichlorethylene (TCE), acetone, and methanol for 5 min each. The degreased wafers were then patterned with an array of 0.5-mm-diam dots using a standard lithographic technique. Prior to metal deposition, the patterned substrates were etched for 2 min by $NH_4OH:H_2O$ (1:2), followed by blow drying with N_2. The Ni_2Al_3 (180 nm)/*n*-GaAs and Ni_2Al_3 (180 nm)/Ni (10 and 16 nm)/*n*-GaAs contacts were made by sputter deposition from two different targets: Ni_2Al_3 and Ni. The NiAl/Al/Ni/*n*-GaAs (Ni:Al=1:1), and Ni/Al/Ni/*n*-GaAs (Ni:Al=3:1, 2:3, and 1:3) contacts were prepared by depositing different thicknesses of Ni, Al, and NiAl. The base pressure of the system was $\sim 2\times10^{-7}$ Torr prior to deposition. The NiAl and Ni_2Al_3 targets with 50 ± 0.03 and 61.69 ± 0.03 at. % Al, respectively, were cold pressed. Annealing of the contacts was carried out

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TABLE I. Schottky barrier heights measured by the I-V method and the ideality factors for the Ni_2Al_3/n-GaAs and Ni_2Al_3/Ni/n-GaAs contacts as a function of annealing condition.

	As-deposited	325 °C/5 min	400 °C/ℓ min	500 °C/20 s
Ni_2Al_3	$\phi_{Bn}^{I\text{-}V}=0.80$	$\phi_{Bn}^{I\text{-}V}=0.808$	$\phi_{Bn}^{I\text{-}V}=0.804$	$n>1.2$
180 nm	$n=1.10$	$n=1.05$	$n=1.10$	
Ni_2Al_3/Ni	$\phi_{Bn}^{I\text{-}V}=0.803$	$\phi_{Bn}^{I\text{-}V}=0.934$	$\phi_{Bn}^{I\text{-}V}=0.95$	$n>1.2$
180/10 nm	$n=1.07$	$n=1.07$	$n=1.10$	
Ni_2Al_3/Ni	$\phi_{Bn}^{I\text{-}V}=0.802$	$\phi_{Bn}^{I\text{-}V}=0.94$	$\phi_{Bn}^{I\text{-}V}=0.96$	$n>1.2$
180/16 nm	$n=1.08$	$n=1.04$	$n=1.08$	

in a rapid thermal annealing furnace in an Ar ambient at 200 °C for 10 min, 325 °C for 5 min, 400 °C for 1 min, 500 °C for 20 s, and 600 °C for 20 s. The back side ohmic contacts were formed either by alloying In onto the n-GaAs substrate at a temperature of 400 °C for 1 min, or by using a Au-Ni-Ge contact. The ohmic contacts were made prior to the Schottky metallization for samples annealed below 400 °C and after metallization for samples annealed above 400 °C.

The Schottky barrier heights were measured at room temperature immediately after the ohmic contacts were made, using the current-voltage (I-V) method and conventional thermionic-emission theory.[10] The relationship between the current and the applied forward voltage is given by

$$I=SA^{**}T^2 \exp[-q(\phi_{Bn}-\Delta\phi_{Bn})/k_BT] \times[\exp(qV/nk_BT)-1], \quad (1)$$

where S is the contact area, A^{**} is the effective Richardson constant (8.64 A/cm^2 K^2 for n-GaAs), k_B is the Boltzmann constant, T is the temperature in K, ϕ_{Bn} is the Schottky barrier height, $\Delta\phi_{Bn}$ is the Schottky barrier lowering [equal to $(qE/4\pi\epsilon_s)^{1/2}$)], E is the maximum electric field at the metal-semiconductor interface, ϵ_s is the permittivity of the semiconductor, and n is the ideality factor. The ideality factor must be close to unity in order to assure that thermionic emission is the dominant transport mechanism. The barrier heights obtained in this study have taken the effect of image force lowering into account.

The interfacial reactions between the contacts and GaAs were examined using cross-sectional transmission electron microscopy (XTEM), glancing angle x-ray diffraction (GAXRD) and scanning Auger microscopy (SAM). XTEM examination of the reacted interfaces was carried out using a JEOL 200 CX.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. The $NiAl_x$/Ni/n-GaAs structure

Values of the SBH and the ideality factors as a function of annealing condition for the Ni_2Al_3/Ni/n-GaAs contacts with two different Ni thicknesses are presented in Table I. The results for the Ni_2Al_3/n-GaAs contacts are also listed in Table I for comparison. The data clearly indicate that the Schottky behavior of all the contacts follows the thermionic-emission model. Ideality factors, less than or equal to 1.1, were determined on structures after annealing at 400 °C for 1 min for all the contacts. The contacts became nonrectifying after being annealed at 500 °C for 20 s, presumably due to defects generated at the metal/semiconductor interface. As shown in Table I, annealing does not enhance SBH of the Ni_2Al_3/n-GaAs contacts. The reacted Ni_2Al_3/Ni/n-GaAs contacts do exhibit an increased SBH, up to 0.95±0.01 eV, regardless of different Ni thicknesses after 400 °C annealing for 1 min. It seems likely that the thin Ni layer plays an important role in ESBH.

Since the annealed Ni_2Al_3/n-GaAs contacts do not exhibit an enhanced SBH, a limited amount of reaction should be expected at the interface. The Auger depth profiles of the contacts, without and with annealing as shown in Figs. 1(a) and 1(b), indicate no detectable reaction at the interface even after annealing at 600 °C for 20 s.

Interfacial reactions did occur for the Ni_2Al_3/Ni/n-GaAs contacts unlike the case of the Ni_2Al_3/n-GaAs contacts. The

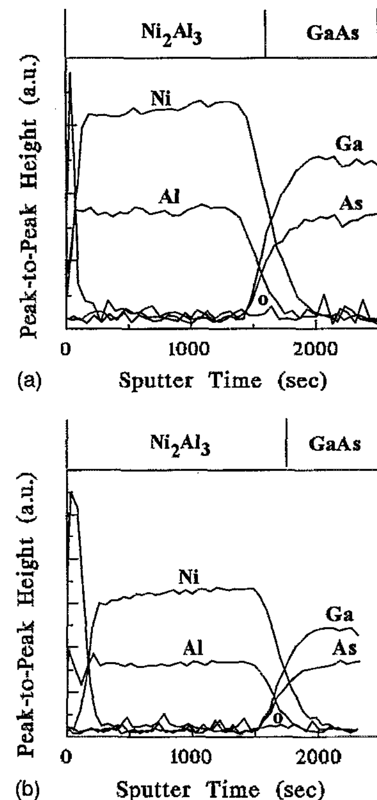

FIG. 1. Auger depth profiles of the Ni_2Al_3/n-GaAs contacts (a) without and (b) with heat treatment at 600 °C for 20 s indicate no detectable reaction at the interface.

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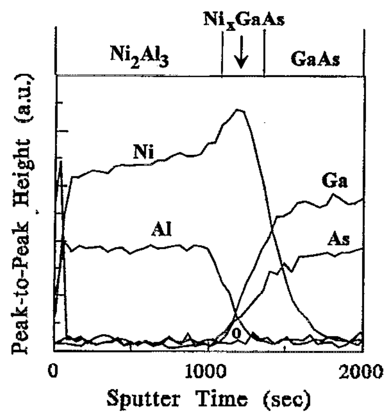


FIG. 2. Auger depth profiles of the Ni_2Al_3/Ni/*n*-GaAs contacts annealed at 200 °C for 10 min indicate the formation of Ni_xGaAs.

Auger depth profile of the contact, annealed at 200 °C for 10 min in Fig. 2, reveals that Ni starts to react with GaAs, forming Ni_xGaAs. The Ni_xGaAs phase has been reported by Lin *et al.*[11] to form at this temperature. According to Colgan *et al.*,[12] Ni does not react with Al until annealing at 300 °C. This implies that Ni will not react with Ni_2Al_3 under the 200 °C annealing for 10 min. The Ni_xGaAs phase may also be seen from a XTEM bright field image of the contacts after heat treatment at 325 °C for 5 min shown in Fig. 3. There are two layers on top of the GaAs substrate. Diffraction analysis of these two layers identified them as Ni_2Al_3 and Ni_xGaAs. Both the Ni_2Al_3 and Ni_xGaAs phases were also observed from the Auger depth profile of contacts prepared under the same annealing condition. The SBH, ~0.94 eV, corresponding to this annealing condition may imply that a thin (Al, Ga)As layer exists between Ni_xGaAs and GaAs. It is, however, difficult to unambiguously determine the presence of (Al,Ga)As. The experimental difficulty is due, in part, to the poor image contrast between (Al,Ga)As and GaAs using a bright field image as well as the thinness of the (Al,Ga)As layer. A contact was annealed at 550 °C for 20 s in order to form a thicker layer of (Al,Ga)As at the interface. The existence of (Al,Ga)As at the interface may be demonstrated using a (200) dark-field XTEM image.[2] The difference between the atomic scattering factor of Al and that of As is significant, while the atomic scattering factors of Ga and As are quite similar. Therefore, the (Al,Ga)As phase would appear bright while the GaAs phase would appear dark in the dark-field image. A bright-field and a (200) dark-field XTEM image of the Ni_2Al_3/Ni/*n*-GaAs contacts, annealed at 550 °C for 20 s, are shown in Figs. 4(a) and 4(b). The (Al,Ga,)As phase is again not detectable in the bright-field image in Fig. 4(a). Nevertheless, Fig. 4(b) shows a bright thin layer formed at the interface, which we presume to be the (Al,Ga)As phase. The presence of this phase would cause the enhancement of Schottky barrier height. The phase in the metal film was verified to be Ni_2Al_3 using the glancing angle x-ray diffraction (GAXRD).

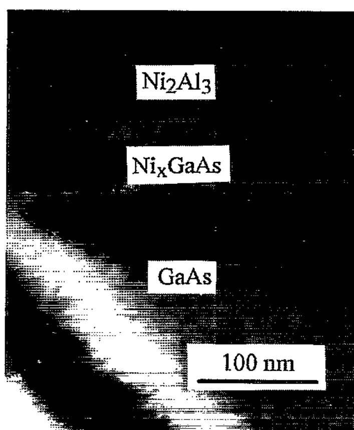
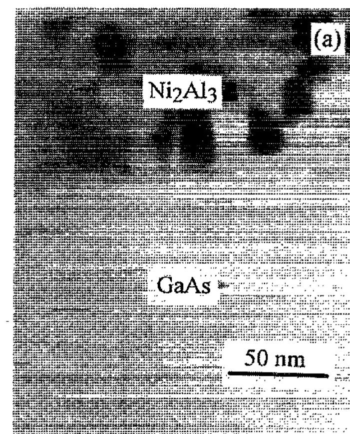


FIG. 3. A bright-field XTEM image of the Ni_2Al_3/Ni/*n*-GaAs contacts annealed at 325 °C for 5 min is used to demonstrate that two reacted layers were on top of GaAs.



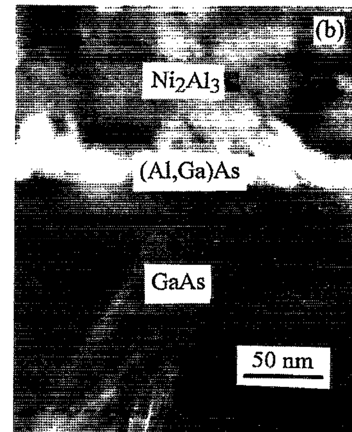


FIG. 4. (a) A bright-field and (b) a (200) dark-field XTEM images of the Ni_2Al_3/Ni/*n*-GaAs contact annealed at 550 °C for 20 s are used to determine the presence of an (Al,Ga)As phase. The (Al,Ga)As phase would be bright and the GaAs phase would be dark on the (200) dark-field image. As shown in (b), a bright thin layer at the interface can be seen in this image, which is assumed to be the (Al,Ga)As phase.

The proposed RM for the Ni_2Al_3/Ni/*n*-GaAs contacts is shown in Fig. 5, based on the interfacial reactions under different annealing conditions described above. Each step in Fig. 5 represents a different heat treatment. As the annealing temperature increases, the structure would change from step (a) through steps (b) and (c) to the final step (d). The overall thin-film concentration is 58% of Al, so the final phase after

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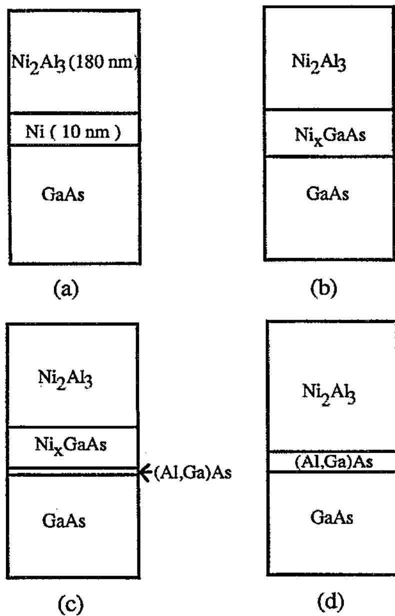

FIG. 5. The proposed regrowth mechanism of the Ni_2Al_3/Ni/*n*-GaAs contacts demonstrates that the contact structure changed from step (a) through step (e) as the annealing temperature increases from room temperature to 550 °C.

annealing at high temperatures is expected to be the Ni-rich Ni_2Al_3 phase. The as-deposited structure is shown as step (a). The structure then becomes Ni_2Al_3/Ni_xGaAs/GaAs, under a low temperature annealing at 200 °C for 10 min [step (b)]. In step (b), the Ni_xGaAs phase forms by reacting Ni with GaAs. Under annealing at 325 °C for 5 min, the structure begins to change as shown in step (c), Ni_2Al_3/Ni_xGaAs/(Al,Ga)As/GaAs. The final contact structure becomes Ni_2Al_3/(Al,Ga)As/GaAs [step (d)]. The formation of (Al,Ga)As is believed to result from the reaction of Ni_xGaAs with the Ni-poor Ni_2Al_3 phase to form (Al,Ga)As and the Ni-rich Ni_2Al_3 phase.

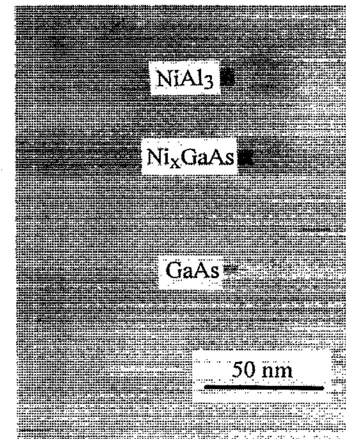

FIG. 6. A XTEM bright-field image of the Ni/Al/Ni/*n*-GaAs (Ni:Al=2:3) contacts annealed at 325 °C for 5 min is used to demonstrate that two reacted layers were on top of GaAs.

B. The $NiAl_x$/Al/Ni/*n*-GaAs structure

The *I-V* measurement results, as a function of annealing temperature for the Ni/Al/Ni/*n*-GaAs (Ni:Al=3:1, 2:3, and 1:3) and NiAl/Al/Ni/*n*-GaAs (Ni:Al=1:1) contacts, are listed in Table II. The transport behavior of all these contacts may be described by the thermionic-emission model. The ESBH, as indicated in Table II, occurs for both of the Ni/Al/Ni/*n*-GaAs (except for Ni:Al=1:3) and NiAl/Al/Ni/*n*-GaAs contact structures. The high SBHs, ~0.98±0.01 eV, for the Ni/Al/Ni/*n*-GaAs structure occurs when the contacts were subjected to annealing at 325 °C for 5 min. The NiAl/Al/Ni/*n*-GaAs contact structure attains a maximum barrier height, 0.95 eV, when annealed at 400 °C for 1 min. The enhanced barrier heights of these two structures may be rationalized in terms of the RM.

A XTEM bright-field image for one of the Ni/Al/Ni/*n*-GaAs (Ni:Al=2:3) contacts annealed at 325 °C for 5 min, as shown in Fig. 6, is used to demonstrate the presence of Ni_xGaAs. Two reacted layers formed on top of the GaAs

TABLE II. Schottky barrier heights measured by the *I-V* method and the ideality factors for the Ni/Al/Ni/*n*-GaAs and NiAl/Al/Ni/*n*-GaAs contact structures as a function of annealing condition.

	As-deposited	325 °C/5 min	400 °C/ℓ min	500 °C/20 s	600 °C/20 s
Ni/Al/Ni (Ni:Al=3:1) 50/33/10 nm	$\phi_{Bn}^{I-V}=0.877$ $n=1.03$	$\phi_{Bn}^{I-V}=0.98$ $n=1.07$	$\phi_{Bn}^{I-V}=0.98$ $n=1.15$	$\phi_{Bn}^{I-V}=0.94$ $n=1.07$	$\phi_{Bn}^{I-V}=0.91$ $n=1.15$
Ni/Al/Ni (Ni:Al=2:3) 10/49/10 nm	$\phi_{Bn}^{I-V}=0.874$ $n=1.04$	$\phi_{Bn}^{I-V}=0.973$ $n=1.08$	$\phi_{Bn}^{I-V}=0.974$ $n=1.21$	$n>1.2$	$n>1.2$
Ni/Al/Ni (Ni:Al=1:3) 10/90/10 nm	$\phi_{Bn}^{I-V}=0.870$ $n=1.03$	$\phi_{Bn}^{I-V}=0.864$ $n=1.07$	$n>1.2$	$n>1.2$	$n>1.2$
NiAl/Al/Ni (Ni:Al=1:1) 100/33/20 nm	$\phi_{Bn}^{I-V}=0.825$ $n=1.05$	$\phi_{Bn}^{I-V}=0.89$ $n=1.06$	$\phi_{Bn}^{I-V}=0.95$ $n=1.14$	$n>1.2$	$n>1.2$
NiAl/Al/Ni (Ni:Al=1:1) 100/16/10 nm	$\phi_{Bn}^{I-V}=0.83$ $n=1.04$	$\phi_{Bn}^{I-V}=0.916$ $n=1.07$	$\phi_{Bn}^{I-V}=0.95$ $n=1.1$	$n>1.2$	$n>1.2$

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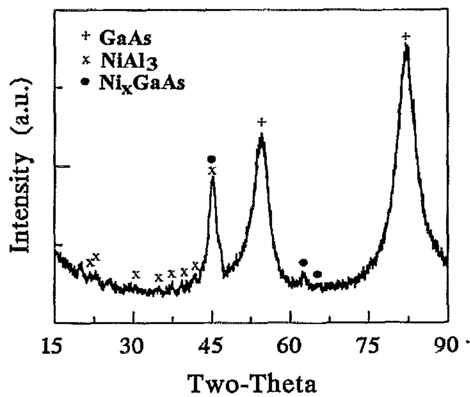

FIG. 7. A glancing angle x-ray diffraction pattern from the Ni/Al/Ni/n-GaAs (Ni:Al=2:3) contacts annealed at 325 °C for 5 min is used to identify that the two reacted layers were $NiAl_3$ and Ni_xGaAs.

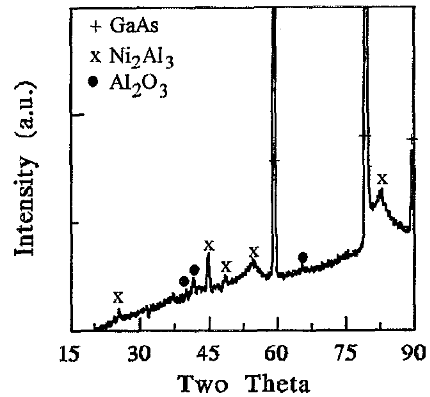

FIG. 9. A glancing angle x-ray diffraction pattern of the Ni/Al/Ni/n-GaAs (Ni:Al=2:3) contacts annealed at 650 °C for 20 s is used to identify the final phase in the contact, which was Ni_2Al_3.

substrate. According to Fig. 7, the GAXRD pattern of these two reacted layers were identified as $NiAl_3$ and Ni_xGaAs. Both $NiAl_3$ and Ni_xGaAs were also observed from the Auger depth profile of contacts subjected to the same heat treatment. The SBH, ~0.97 eV, corresponding to this annealing condition implies that a thin (Al,Ga)As layer may exist between Ni_xGaAs and GaAs. The (Al,Ga)As phase cannot again be seen in Fig. 6, as indicated above. A (200) dark-field XTEM image of a contact after annealing at 650 °C for 20 s in Fig. 8 is used to demonstrate the existence of (Al,Ga)As. A thin bright layer at the interface can be seen in this image which is assumed to be the (Al,Ga)As phase.

The formation of (Al,Ga)As can be explained by the reaction of the Ni_xGaAs phase with the top layer, the $NiAl_3$ phase. Free Ni atoms may also be generated and diffuse either to form the Ni-rich Ni_xGaAs phase or to dissolve in the (Al,Ga)As phase. It is likely that the free Ni atoms can diffuse farther into the GaAs substrate when the structure is subjected to high temperature anneals. An appreciable solubility of Ni in GaAs at 600 °C has been reported.[7] The degradation of contacts at 500 °C for 20 s annealing may result from the diffusion of Ni atoms into GaAs at that temperature. The final reaction product in the thin film is Ni_2Al_3, which can be determined from the GAXRD pattern shown in Fig. 9.

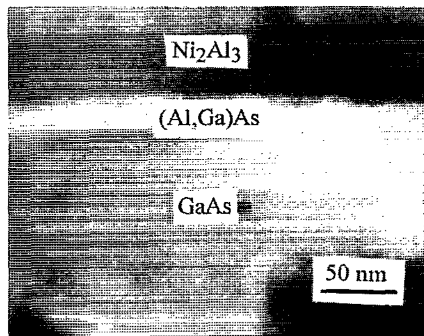

FIG. 8. A (200) dark-field XTEM image of the Ni/Al/Ni/n-GaAs (Ni:Al =2:3) contacts annealed at 650 °C for 20 s is used to discern the presence of a (Ga,Al)As phase. The (Ga,Al)As phase would be bright and the GaAs phase would be dark on this dark-field image.

Some peaks corresponded to Al_2O_3 phase, possibly because the sample surface became oxidized after a high temperature annealing. The evidence of surface oxide can also be seen from an Auger depth profile of the contacts annealed at the same temperature.

Figure 10 shows a proposed RM for the reacted Ni/Al/Ni/n-GaAs (Ni:Al=2:3) contacts, involving a total of five steps. Each step, again, represents a different heat treatment with the structure changing from step (a) to (e) as the annealing temperature increases. The overall thin-film concentration is 60% Al, so the final phase after annealing at a high enough temperature is expected to be Ni_2Al_3. The as-deposited structure is shown as step (a). Under a low temperature annealing at 200 °C for 10 min, the structure became Ni/Al/Ni_xGaAs/GaAs, which is step (b). The reaction

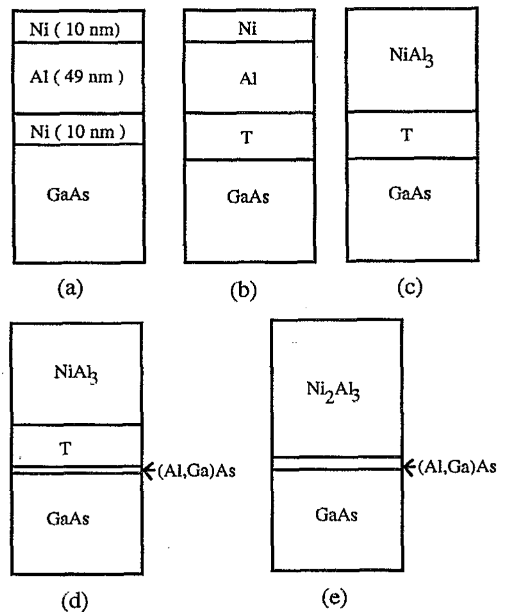

FIG. 10. The proposed regrowth mechanism of the Ni/Al/Ni/n-GaAs (Ni:Al =2:3) contacts demonstrates that the contact structure changed from step (a) through step (e) as the annealing temperature increases from room temperature to 650 °C.

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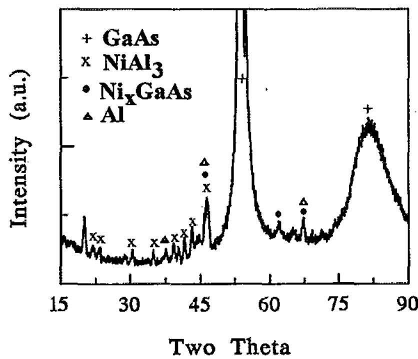

FIG. 11. A glancing angle x-ray diffraction pattern of the Ni/Al/Ni/n-GaAs contacts with 75 at. % Al in the film annealed at 325 °C for 5 min shows the existence of Al, $NiAl_3$, and Ni_xGaAs.

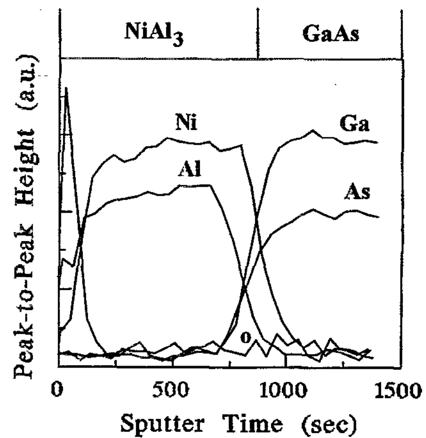

FIG. 12. Auger depth profiles of the Ni/Al/Ni/n-GaAs contacts with 75 at. % Al in the film annealed at 400 °C for 1 min exhibit the final contact structure: $NiAl_3$/n-GaAs.

of this step is similar to that described in Sec. III A. The structure may change first to $NiAl_3$/Ni_xGaAs/GaAs [step (c)] and then to $NiAl_3$/Ni_xGaAs/(Al,Ga)As/GaAs [step (d)] after annealing at 325 °C for 5 min. The existence of (Al,Ga)As corresponds to a high SBH obtained when the contacts are annealed at 325 °C for 5 min. After annealing at 650 °C for 20 s, the final structure would be Ni_2Al_3/(Al,Ga)As/GaAs, which is step (e). Step (e) results from the reaction of $NiAl_3$ with Ni_xGaAs to form Ni_2Al_3 and (Al,Ga)As.

The annealed Ni/Al/Ni/n-GaAs contacts with 75% Al in the film did not enhance the barrier height. Even though Ni_xGaAs started to form after annealing at 200 °C for 10 min, this phase did not react with Al when annealed at 325 °C for 5 min. Figure 11 shows the coexistence of Al and Ni_xGaAs. The formation of $NiAl_3$ is due to the reaction between a portion of Al layer and the Ni overlayer. When contacts were subjected to heat treatment at 400 °C for 1 min, the Auger depth profiles in Fig. 12 indicate the final contact structure changed to $NiAl_3$/n-GaAs. The absence of (Al, Ga)As in the contacts was attributed to a kinetic constraint. The $NiAl_3$ phase forms so fast by reacting Al and Ni_xGaAs that there is insufficient time for the formation of (Al,Ga)As.

IV. CONCLUSIONS

Contacts with enhanced Schottky barrier heights have been realized using the Ni_2Al_3/Ni/n-GaAs, Ni/Al/Ni/n-GaAs (Ni:Al=1:3 or 2:3) and NiAl/Al/Ni/n-GaAs structures fabricated by sputter deposition at a base pressure of $\sim 2\times 10^{-7}$ Torr. A high Schottky barrier height ranging from 0.95 to 0.98 eV (deduced from the I-V measurements) was observed for all the above annealed contacts. The enhanced Schottky barrier height was attributed to the formation of a thin (Al, Ga)As layer at the metal/semiconductor interface. The results were rationalized in terms of a regrowth mechanism.

ACKNOWLEDGMENTS

The authors wish to thank Dr. M. Dahms of GKSS, Geesthacht, Germany for making the NiAl and Ni_2Al_3 sputtering targets for us. The authors also wish to thank D. Swenson for reviewing this manuscript. The financial support of the Department of Energy through Grant No. DE-FG02-86ER452754 is gratefully acknowledged.

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