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Development of Electrode Materials for Semiconductor Devices

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Recent strong demands for optoelectronic communication and portable telephones have encouraged engineers to develop optoelectronic devices, microwave devices, and high-speed devices using heterostructural compound semiconductors. Although the compound crystal growth techniques had reached at a level to control the compositional stoichiometry and crystal defects on a nearly atomic scale by the advanced techniques such as molecular beam epitaxy and metal organic chemical vapor deposition techniques, development of ohmic contact materials (which play a key role to inject external electric current from the metals to the semiconductors) was still on a trial-and-error basis. Our research efforts have been focussed to develop, low resistance, refractory ohmic contact materials using the deposition and annealing techniques for n-GaAs, p-ZnSe, InP, p-SiC p-CdTe etc. It was found the growth of homo- or hetero–epitaxial intermediate semiconductor layers (ISL) was essential for low resistance contact formation. The importance of hetero-structural ISL was given taking an example of n-type ohmic contact for GaAs.

Key words: ohmic contact, compound semiconductor, regrowth, intermediate semidconductor layer

1. Introduction

Gallium arsenide compound semiconductor has the intrinsic electrical properties superior to Si semiconductor, including higher electron mobility, direct energy bandgap, and lower power dissipation. These advantages of GaAs are attractive to develop high-speed very large-scale integrated electronic devices, optoelectronic devices, and discrete microwave electronic devices. Specially, recent strong world-wide demand for portable telephones motivated us to develop the high frequency devices with lower power dissipation.

Although there are several advantages of GaAs over Si as described above, the materials properties of GaAs, such as high defect density, and poor mechanical properties, are inferior to those of Si. These poor properties of GaAs are simply due to the fact that GaAs is composed of two elements and the control of the perfect chemical stoichiometry of Ga and As is extremely difficult. Also, difficulty to control the concentrations of electrically active donors and acceptors is caused by existance of two different vacancy sites of Ga and As sites.

There have been intensive research and development efforts to grow GaAs-based semiconductors using molecular beam epitaxy (MBE), mental organic chemical vapor deposition (MOCVD), and liquid-encapsulated-Czochralski (LEC) techniques. These growth techniques combined with the post-annealing technique reduced significanty the lattice defects incorporated unintensionally in GaAs during crystal growth and succeeded to control the composition and hetero-structural layer on an atomic scale. However, ohmic contact materials which are key elements for GaAs devices have been, unfortunately, developed on a trial-and-error basis.

The primary purpose of the present article is to review extensively recent progress of ohmic contact materials for GaAs devices, which have been carried out mainly in our laboratories based on materials science.

2. Guideline for low resistance ohmic contact formation

The best way to modify the interfacial microstructure to produce low resistance ohmic contact is to form a new intermediate semiconductor layer (ISL) at the metal/semiconductor interface as shown in Fig.1. This ISL must be grown epitaxially on the base semiconductor. There are two kinds of ISL's which would reduce the contact resistance. The one is a homo-epitaxial ISL which contains a high density of carriers. The other is a hetero-epitaxial ISL which has a low energy barrier at the metal/ISL interface, small band off-set, and small lattice mismatch with the base compound semiconductor.

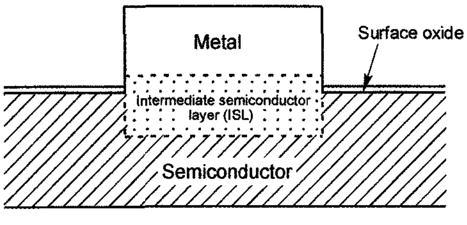

Fig. 1 . Cross-section of metal/semiconductor interface with intermediate semiconductor layer (ISL).

The energy band diagrams of these semiconductors which contain homo- and hetero-epitaxial ISL are shown in Figs. 2(a) and 2(b), respectively[1,2]. These diagrams give us guidelines to design the ideal M/S interfacial structure for low resistance ohmic formation. The conventional ohmic contact preparation technique involves deposition of the contact metal(s) onto the cleaned GaAs substrate and annealing the contacts at elevated temperature to form ISL at the metal / GaAs interface. Low resistance ohmic contacts are prepared, when the ISL with low energy barrier or high carrier density is formed between the metal(s) and the semiconductor after heat-treatment as shown in Fig. 2. The contacts prepared by this fablication process are named as "DA (Deposition and Anneal) ohmic contacts". The present article will review the contact properties of the ohmic contacts developed in our laboratories by the DA technique based on concept of Fig.2(b).

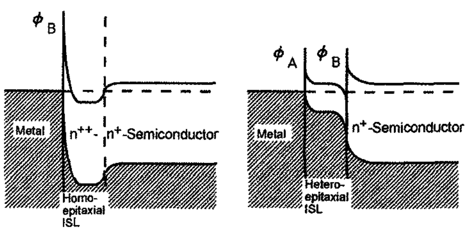

Fig. 2 . Energy band diagrams of metal/semiconductor interfaces with highly doped ISL (a) and low energy barrier ISL (b) .

3. Development of ohmic contact materials with hetero-epitaxial ISL

Reduction of the R_C value to a level of $10^{-6}\Omega\cdot cm^2$ for n-GaAs was achieved by formation of hetero-epitaxial ISL with "low Schottky barrier" at the metal/GaAs interface after annealing at elevated temperatures. The best candidate as such the intermediate semiconductor layer (ISL) for n-GaAs was n-type $In_xGa_{1-x}As$, which has an energy gap and Schottky barrier less than those of GaAs. The energy gaps and the barrier heights of n-type $In_xGa_{1-x}As$ were measured by Kajiyama et al [3]. The energy gap (E_g) of $In_xGa_{1-x}As$ became narrower with increasing the In concentration (x) in the $In_xGa_{1-x}As$ and was measured to be 0.4 eV for InAs. The barrier height (ϕ_B)at the metal/n- $In_xGa_{1-x}As$ decreased with increasing the In concentration (x) in the $In_xGa_{1-x}As$ and became zero at x=0.7. In addition, the maximum lattice mismatch between $In_xGa_{1-x}As$ and GaAs is about 7%. This relatively small mismatch indicated a possibility of epitaxial growth of an $In_xGa_{1-x}As$ layer on the GaAs surface. Within our knowledge, this $In_xGa_{1-x}As$ is only semiconductor that reduces the barrier height at M/S interface with small lattice mismatch with GaAs.

The feasible energy band diagram at the metal/ $In_xGa_{1-x}As$/GaAs interface constructed based on the energy gap measurement of $In_xGa_{1-x}As$ is schematically shown in Fig. 2(b), where the hetero-epitaxial ISL corresponds $In_xGa_{1-x}As$ ISL [2]. There are two energy barriers for electron transport through this interface; one is the energy barrier (ϕ_A) between metal and $In_xGa_{1-x}As$ and the other is the energy barrier (ϕ_B) between $In_xGa_{1-x}As$ and GaAs. When a metal contacted directly to GaAs, the value of (ϕ_A) was measured to be close to 0.8 eV. The R_C value at the GaAs / $In_xGa_{1-x}As$ / metal interface was determined by the series resistances through these two barriers. As described above, the ϕ_A value decreased with increasing the x value in the $In_xGa_{1-x}As$ layer. However, the lattice parameter of the ternary layer decreased with increasing the In concentration and the lattice mismatch at the $In_xGa_{1-x}As$/GaAs interfaces increased. The barrier ϕ_B was associated with band gap discontinuities and the interface states were related to the lattice mismatch. The ϕ_B value increased with increasing the In concentration in the $In_xGa_{1-x}As$ layer, which led to an increase in the R_C value. Therefore, there was an optimum In concentration in the intermediate $In_xGa_{1-x}As$ layer shown in Fig. 2(b).

There were two techniques (extensively used to fabricate commercial GaAs devices) to form these $In_xGa_{1-x}As$ layers at the metal/GaAs interfaces. The one was the sputter-deposition technique using $In_xGa_{1-x}As$ targets and the other was the vacuum evaporation technique using a small amount of In as evaporating materials. The low resistance ohmic contact materials prepared by these techniques will be given below.

4. Development of $In_xGa_{1-x}As$-based ohmic contact materials by the sputtering technique

The $In_xGa_{1-x}As$/Ni/W ohmic contacs with various x values were prepared [4,5]. Since $In_{0.7}Ga_{0.3}As$-based contacts provided low resistance, the results on this contacts will be given below. The substrates used in the present experiments were semi-insulating (100)-oriented GaAs. The conducting channels for TLM were made on the GaAs substrate doped with Si at $2\cdot10^{18}cm^{-3}$. Prior to deposition, the GaAs(100) substrates were chemically cleaned by rinsing in HCl for 3 min and deionized water for 1 min. The samples ($In_{0.7}Ga_{0.3}As$ /Ni/W) were sequentially deposited by the rf sputtering technique. The $In_{0.7}Ga_{0.3}As$ layers were sputter-deposited by Ar using $In_{0.7}Ga_{0.3}As$ targets in the base pressure of 4×10^{-5} Pa. The deposition rate was about 0.1 nm/s. The In, Ga, and As compositions in the $In_{0.7}Ga_{0.3}As$ layers were analyzed by electron probe micro analysis (EPMA). The compositions in the films were close to those in the targets within experimental errors. Ni and W layers were subsequently sputter-deposited by Ar in the same base pressure. The deposition rates of the Ni and W were about 0.1 and 0.06 nm/s, respectively. The thicknesses of the $In_{0.7}Ga_{0.3}As$ layers were in the range of 20-40 nm, and the Ni layer thicknesses were in the range of 10-20 nm. The W layers with 50 nm thick covered these contact layers. After deposition, the photo-resists were lifted off.

The contact resistance (R_C) values are plotted in Fig.3 as a function of annealing temperatures, where the contribution of the metal sheet resistance to the contact resistance was substracted using an equation given by Marlow and Das [6]. (In this figure, the R_C values of the InAs/Ni/W [4] are shown for comparison.) The lowest value ~0.4Ω·mm of the contact resistance was obtained after annealing at 600°C. The optimum temperature to produce the lowest contact resistance was decreased by 150°C in the $In_{0.7}Ga_{0.3}As$ /Ni/W contacts compared with that of the InAs/Ni/W contacts. However, the temperature range to provide the R_C values less than 0.6Ω·mm was narrower for the $In_{0.7}Ga_{0.3}As$/Ni/W contacts compared with that of InAs/Ni/W contacts.

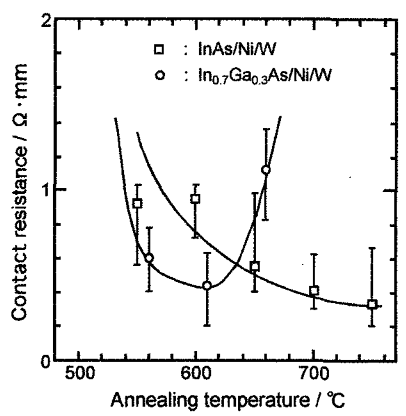

Fig. 3. Contact resistances of the $In_{0.7}Ga_{0.3}As$/Ni/W contact (shown by circles) annealed at various temperatures by RTA.

In order to obtain a guideline to reduce the contact resistances of $In_xGa_{1-x}As$-based ohmic contacts, the electrical properties and the microstructures of the contacts were correlated for the $In_{0.7}Ga_{0.3}As$/Ni/W contacts which were pre-annealed at 300°C for 30 min and then subsequently annealed at 400~800°C for 1 s.

The interfacial reaction of the $In_{0.7}Ga_{0.3}As$ / Ni / W contacts was first studied by x-ray diffraction. In the as-deposited sample, the $In_{0.7}Ga_{0.3}As$ layer was observed to have an amorphous structure. After annealing at 300°C for 30 min, Ni reacted with the $In_{0.7}Ga_{0.3}As$ layer and the peaks corresponding to $NiAs_2$ were detected. Crystallization of the $In_{0.7}Ga_{0.3}As$ layer was observed at 500°C and this layer reacted with the GaAs at higher temperatures. The In composition(x) in the $In_xGa_{1-x}As$ layer was about 0.7 for the contacts annealed at temperatures in the range of 500 to 600°C and decreased to 0.5 at the temperatures above 600°C. Note that the lowest contact resistance was obtained in the contact annealed at 600°C.

The microstructures of the $In_{0.7}Ga_{0.3}As$ / Ni / W contacts were also studied by TEM. The coexistence of the amorphous $In_{0.7}Ga_{0.3}As$ layers and the crystalline $NiAs_2$ layers was observed at the Ni and GaAs interface in the contact annealed at 300°C. After annealing at 600°C, the partial reaction between the $In_{0.7}Ga_{0.3}As$ and the GaAs was observed and the $In_{0.7}Ga_{0.3}As$ layers were observed to cover 30~60% of the GaAs surface. High resolution lattice images at the GaAs/ $In_{0.7}Ga_{0.3}As$ interface and at $In_{0.7}Ga_{0.3}As$/NiAs interface of this contact showed the three compound layers (GaAs, $In_{0.7}Ga_{0.3}As$, NiAs) which were determined by the spacings of the lattice images. The $In_{0.7}Ga_{0.3}As$ layers were observed to grow epitaxially on the GaAs substrate and the NiAs layers were found at the $In_{0.7}Ga_{0.3}As$ and GaAs interfaces after annealing at 600°C, which agreed well with the XRD results.

The In concentrations (x) in the $In_xGa_{1-x}As$ layers were measured by the spacings of the lattice images of the $In_xGa_{1-x}As$ layers. It was found that the In concentrations(x) in the $In_xGa_{1-x}As$ layer at the metal/$In_xGa_{1-x}As$ interface were higher than those at the GaAs/$In_xGa_{1-x}As$ interface. The correlation between the In concentrations(x) in the $In_xGa_{1-x}As$ layers and the R_C values indicated that the low resistance contacts required the high In concentrations (x~1.0) at the metal/$In_xGa_{1-x}As$ interface and the low In concentration (x~0.5) at the $In_xGa_{1-x}As$/GaAs interface of the $In_xGa_{1-x}As$/Ni/W contacts.

The surface morphology of the $In_{0.7}Ga_{0.3}As$/Ni/W contact was observed by optical microscopy. The surface of the contact which provided the lowest contact resistances by annealing at 600°C for 1 s improved compared with that of the InAs/Ni/W contact, but was still rough. In addition, this contact showed poor reproducibility of the low R_C values. These poor properties were found to be due to In out-diffusion through the W cap layer, because the contacts were annealed at temperatures much higher than the melting point of In. Therefore, a new cap layer which prevents the In outdiffusion must be developed to improve these poor properties.

5. Development of In-based ohmic contact materials by the eveporation technique

The important issues to prepare In-based ohmic contact materials by the evaporation techniques were (1) growth of $In_xGa_{1-x}As$ layers on the GaAs substrate by reaction of In and GaAs at elevated temperatures, (2) thermal stability of In-based ohmic contacts after contact formation, and (3) selection of contact metals which produced thermally stable, low resistance contacts (other than In). These issues will be addressed below.

In order to address the first issue of the formation of $In_xGa_{1-x}As$ layer by In and GaAs reaction, the reaction between (pure) In and GaAs was examined theoretically and experimentally. The In and GaAs interactions at high temperatures were predicted by phase diagrams before experiments were carried out by XRD and TEM. Ternary InGaAs phase diagrams were calculated [7,8] using an equation given by Antypas [9], where the activity coefficient in the liquid phase was calculated using Darken's quadratic equation [10] and the solid solution in equilibrium with the ternary liquid was assumed to be regular. An example of a phase diagram calculated at 700°C is shown in Fig.4 [7]. The dashed lines indicate tie-lines which connect two thermal equilibrium phases at 700°C. At this temperature the solid $In_xGa_{1-x}As$ phase and the liquid In (Ga,As) phase (indicated by points *a* and *b*, respectively) coexist when the "effective" average composition is at the point *c* which is within the two phase region.

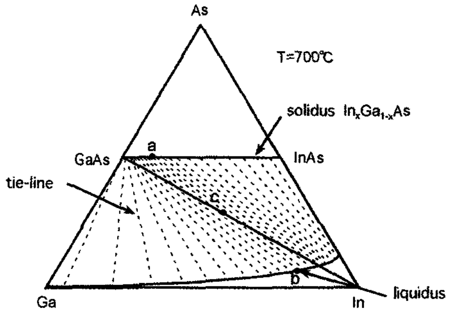

Fig. 4. Ternary InGaAs phase diagram calculated at 700°C.

The coexistence of two phases after annealing In/GaAs contacts was confirmed by TEM observation. The microstructures of In deposited on GaAs were observed by Ding et al [11] and Kim et al [7]. A high-resolution cross-sectional TEM micrograph of the In/GaAs contact showed that no interaction between In and GaAs was observed in an as-deposited sample. A thin oxide layer observed at the interface prevented the In and GaAs reaction. After annealing at 700°C, the $In_xGa_{1-x}As$ layers were observed to be epitaxially grown locally on the GaAs substrate. No misfit dislocations were observed at the $In_xGa_{1-x}As$/GaAs interfaces. This indicated that the In concentration, x, in the $In_xGa_{1-x}As$ layer was small. The selected area diffraction (SAD) analysis on the $In_xGa_{1-x}As$ layer also indicated that the composition of the $In_xGa_{1-x}As$ layer was close to GaAs. The In concentrations (x) of the $In_xGa_{1-x}As$ layers were determined by EDX for the contacts annealed at various temperatures, and their x values were smaller than 0.4. This experimentally determined x value agreed very well with that calculated from the InGaAs phase diagram.

Based on the ideal interfacial structure shown in Fig. 5, NiInGe ohmic contact materials were developed [12]. Ni was selected as the key contact element, because Ni formed refractory intermetallic compounds with In and was expected to improve thermal stability. Ge was selected, because Ge doped heavily the GaAs surface through the regrowth mechanism and was expected to contribute to reduce the contact resistance in addition to reduction of the barrier height by $In_xGa_{1-x}As$ formation.

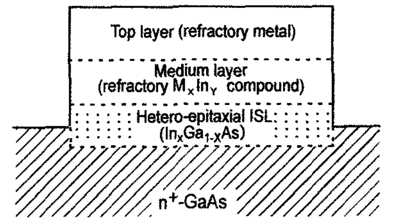

Fig. 5. Cross-section of ideal In-based ohmic contact.

The NiInGe contacts were prepared by the following procedures. The GaAs substrates doped with $2\times10^{18}cm^{-3}$ Si were loaded into a vacuum evaporation system equipped with a cryopump, which was pumped down to ~6.0×10^{-7} Torr before metal deposition. Ni and Ge were evaporated using an electron beam and In was evaporated by a resistance heater. Contact materials with layered structures of GaAs/Ni/In/Ge with various layer thicknesses were prepared [12]. After metal deposition, the samples were lifted-off, and then annealed at temperatures ranging from 450 to 700°C in a rapid thermal annealer (RTA) for 5 seconds in a 5% H_2/N_2 atmosphere.

The contact resistances (R_C) were measured using a TLM, and the lowest R_C value of 0.18Ω-mm was obtained for the Ni(18 nm)/In(13nm)/Ge(30 nm) contact after annealing at temperature of 650°C for 5 sec. The R_C values were found to be affected strongly by the process parameters such as thicknesses of Ni, In, and Ge layers, annealing temperatures and time. These process parameters were believed to affect the microstructure at the metal/GaAs interface, which controlled the R_C value.

In order to correlate the R_C values and the interfacial microstructures, microstructures of the NiInGe contacts prepared by various processes were analyzed by X-ray diffraction. The peaks corresponding to $In_xGa_{1-x}As$ layers were found in the contacts which were annealed at elevated temperatures. The volume fractions of the $In_xGa_{1-x}As$ layers were measured by integrating the peak intensities diffracted from $In_xGa_{1-x}As$ compounds, and the average In concentrations(x) were determined by the peak positions. In the transmission electron microscopic study, it was observed that the $In_xGa_{1-x}As$ layers were grown epitaxially on the GaAs substrates.

The R_C values were measured for the NiInGe contacts with various Ni, In, and Ge layer thicknesses and correlated with microstructures of the $In_xGa_{1-x}As$ layers analyzed by XRD. The R_C values were found to depend on both the volume fraction and the In concentration (x) of the $In_xGa_{1-x}As$ layers, and the R_C values of the contacts are plotted in Fig. 6 as functions of both the volume fraction (relative integrated intensities) and the In concentration(x) of the $In_xGa_{1-x}As$ layers. The low R_C values were obtained in the contacts which formed the $In_xGa_{1-x}As$ layers with the large volume fraction and the In concentrations (x) smaller than 0.6.

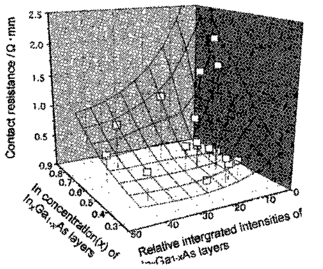

Fig. 6 . Contact resistances as functions of In concentration and volume fraction of $In_xGa_{1-x}As$ layers .

Detailed microstructural analysis of the NiInW contacts which provided low contact resistances was carried out. For these contacts, the broad peaks were measured, indicating coexistance of the $In_xGa_{1-x}As$ layers with various In concentrations. In order to determine these In concentrations the XRD profile of the NiInGe contact annealed at 650°C was deconvoluted with four X-ray profiles. These profiles corresponded to the $In_xGa_{1-x}As$ layers with In concentrations in the range of 0.4 to 0.9. These layers were grown on the GaAs surface as shown schematically in Fig. 7(a). The R_C values were found to be strongly influenced by the $In_xGa_{1-x}As$ layers with smaller In concentrations.

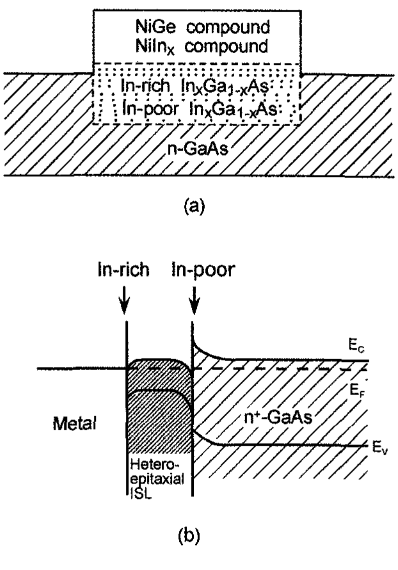

Fig. 7 . Microstructure at the metal/GaAs interface of NiInGe contact which provided low R_C (a) and the corresponding band diagram(b).

Based on the microstructural analysis, the energy band diagram of the NiInGe contact which provided the low R_C value is schematically illustrated in Fig. 7(b). There were two energy barriers at the metal/GaAs interface of the contacts which formed the $In_xGa_{1-x}As$ layers on the n-type GaAs as ahown in Fig. 2(b). The one was the energy barrier (ϕ_A) at the interface between the n- $In_xGa_{1-x}As$ and the contact metal, and the other was the energy barrier (ϕ_B) at the interface between the n-GaAs and n-$In_xGa_{1-x}As$. The R_C value was controlled by these two barriers. However, the present NiInGe contacts were found to form the $In_xGa_{1-x}As$ layers with various In concentrations in the range of 0.4 to 0.9, and the R_C values were found to have strong dependence on the In concentrations of the $In_xGa_{1-x}As$ layers close to the GaAs substrate. Since the $In_xGa_{1-x}As$ layers close to the metal were found to have the In concentrations higher than 0.7, the ϕ_A values were almost zero and would not control the R_C values of the present NiInGe contacts. Thus, the R_C values were believed to be determined by the barrier height ϕ_B at the interface between the GaAs and $In_xGa_{1-x}As$ layers. This ϕ_B value would be determined by the lattice misfit between the GaAs and $In_xGa_{1-x}As$ layers. The R_C values were reduced with decreasing density of misfit dislocations at the n-GaAs/n-$In_xGa_{1-x}As$ interfaces by reducing the lattice mismatch between the two semiconductors. This experiment indicated that formation of the $In_xGa_{1-x}As$ layers with the In concentration(x) less than 0.6 close to the GaAs surface was needed to obtain the low R_C values. It was also found that the R_C values of the NiInGe contacts were reduced by increasing the total area of the GaAs surface covered by the $In_xGa_{1-x}As$ layers as explained in the previous experimental results for In-based ohmic contacts [2].

Therefore, it was believed that the $In_xGa_{1-x}As$ layers with various In concentrations (x) had low "effective" barrier height at both the n-GaAs/n-$In_xGa_{1-x}As$ interface and the n-$In_xGa_{1-x}As$/NiGe interface as shown in Fig. 7(b). Such the contacts with the various In concentrations(x) normal to the GaAs surface could be prepared by rapid heating of the contacts at elevated temperatures for a short time, which provided "incomplete" chemical reaction between the NiInGe and GaAs.

6. Summary

Refractly ohmic contact materials with low contact resistances for n-type GaAs were developed by using the deposition and annealing techniques. These contact materials provided excellent thermal stability, smooth surface morphology, and shallow diffusion depth superior to those of AuGeNi contact materials which have been commercially used in GaAs devices for over 30 years.

To prepare such the low resistance contact materials, formation of an intermetallic semiconductor layer (ISL) at the metal/GaAs interface was found to be essential. Two types of ISL were found to contribute reduction of the contact resistance. The one was homo-epitaxial ISL which was formed by the regrowth mechanism of a new GaAs layer on the GaAs substrate. Enrichment of the doping concentration of donors in the ISL was successfully made by addition of small amounts of elements which had strong binding energy with Ga and weak energy with As. These homo-epitaxial ISL produced the refractory NiGe-based ohmic contact materials using the evaporation techniques. The other type of ISL was hetero-epitaxial ISL which was formed by deposition of a narrow gap semiconductor such as InAs or $In_xGa_{1-x}As$ on GaAs or by chemical reaction of In and GaAs. It was found that reduction of Schottky barrier height by the ISL formed at the metal/n-GaAs was made only when the ISL had the In concentration gradient : In being rich close to the metal contact and poor close to the GaAs surface. To form such the In concectration graded ISL, the metastable reaction between In (or $In_xGa_{1-x}As$) and GaAs was needed which made the process window (to provide low contact resistance) narrower. $In_xGa_{1-x}As$-based and In-based ohmic contact materials were successfully developed by discovering the optimum fabrication process windows.

To improve thermal stability, refractory metals or intermetallic compounds were needed as the cap layers which prevented the out-diffusion of key elements needed to form homo- or hetero-epitaxial ISL. In addition, removal of low melting point compounds or phases from the contact interfaces was also needed to prepare thermally stable contacts.

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