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The Formation and Phase Stability of Cobalt-aluminide (CoAl) Thin Films on GaAs

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We have investigated the formation and thermal stability of cobalt aluminide (CoAl) thin films on GaAs. In order to obtain cobalt-aluminide thin films, we deposited a multilayer of Co/Al on GaAs, and subsequently annealed the samples at 800°C for 30 min. After annealing, single-phase cobalt aluminide was produced showing a flat and uniform interface with GaAs, which indicates that cobalt aluminide (CoAl) is thermally stable with GaAs. In addition, the adherence and mechanical properties of the as-deposited, and annealed Co/Al multilayer structure on GaAs are compatible with those required for device fabrication processes. The electrical property of the CoAl/GaAs contact shows rectifying characteristics, indicating that the diodes were usable as rectifying gate electrodes.

Key words : Cobalt aluminide (CoAl), Self-aligned gate GaAs MESFET, Thermal stability, Gate electrode, Barrier height

I. Introduction

A high-temperature stable metallization is an especially critical issue for the self-aligned gate GaAs metal-semiconductor field-effect-transistor (MESFET) process.[1] This technology uses the same gate structure as a mask during n^+ implantation into the source and drain regions, and, thus, offers simpler processing steps and compatibility with future scaling of GaAs integrated circuits. Further processing involves a high temperature annealing, typically at 800°C-830°C for 10 -20 minutes furnace-annealing, or at 900°C for 10-20 seconds rapid-thermal-annealing. This process is necessary to activate the implanted dopants and to remove implantation damages in the source and drain regions of the GaAs substrate. Therefore, the gate materials should maintain a reproducible rectifying property and have a geometrically flat interface with the channel region under the gate after high-temperature annealing processes. For this purpose, a number of materials including elemental metals and intermetallic compounds, have been tested. As most of the elemental metals severely react with the GaAs substrate upon annealing even at low temperature, they are not suitable for this application.[2-5] Some elements such as Ag, Au, and W are thermodynamically stable with GaAs according to the ternary phase diagram. However, they have other problems such as stress in the film, solid-solution, or melting upon high temperature annealing.[1,2,6,7] Therefore, intermetallic compounds that are thermally as well as electrically stable on GaAs, should be used.

As thermally stable intermetallic compounds on GaAs substrates, metal-aluminides are suggested by the following reasons: (1) The metal-aluminide may show chemical properties similar to those of the corresponding metal-gallide because the isovalent element Al takes the phase of Ga in those metal-gallides that are stable; their stability can be determined form the metal-Ga-As ternary phase diagram; (2) Metal-aluminides often have a large negative free energy of formation (and so a high melting point), which can be an indication of their thermal stability; (3) Metal-aluminides generally have low resistivity, which is another criterion for gate materials; (4) Most importantly, metal-aluminides can be fabricated by conventional vacuum deposition techniques such as electron beam deposition or sputtering. Among several metal-aluminides that meet these conditions we suggest cobalt-aluminides as gate electrode materials for high temperature stable metallization systems. Cobalt aluminide is a thermodynamically stable compound (with a Gibbs free energy of formation of kcal/mole, and a melting point of 1645°C,[8,9]) and it substitutes the isovalent element Al for Ga in CoGa which has been proved to be thermodynamically stable with GaAs by thin film experiments.[10,11] In addition, cobalt aluminide may show an epitaxial relationship with GaAs. The formation of an epitaxial metallic layer is important because it allows the fabrication of a wide range of novel electronic and photonic device structures based on metal/compound-semiconductor heterojunctions (e.g., metal-base and transistors).[12,13] Investigations of Co/GaAs reactions have shown that CoGa, which is cubic (CsCl structure), is produced, showing epitaxy with GaAs.[10] Since cobalt aluminide also adopts the cubic CsCl structure, with a lattice parameter of 2.861 Å (1.2% misfit with GaAs), which is nearly identical to the lattice parameter of CoGa (2.878 Å, 1.8% misfit with GaAs), it may also be formed epitaxially on GaAs like nickel aluminides.[11,15]

In this paper, we discuss the formation and thermal stability of cobalt aluminides on GaAs. In order to obtain cobalt aluminide thin films, we deposited a multilayer of Co/Al on GaAs, and subsequently annealed the samples. We found that a single-phase cobalt aluminide was produced showing a flat and uniform interface with GaAs after annealing, which indicates that cobalt aluminide is thermally stable with GaAs. In addition, the adherence and mechanical properties of the as-deposited, and annealed Co/Al multilayer structures on GaAs are compatible with those required for device fabrications. The electrical property of the CoAl/GaAs contact shows rectifying characteristics, indicating that the diodes were usable as rectifying gate electrodes.

II. Experiments

(100)-insulating GaAs wafers were chemically cleaned prior to the metal deposition for the removal of chemical residues such as native oxide and hydrocarbon. Cleaning procedures include treatments in boiling trichloroethylene for 10 min, in acetone for 1 min, in boiling isopropyl alcohol for 15 min for the removal of organic materials on the surface, and in a H_2O_2:H_2O:H_2SO_4 (1:1:5) solution for 1 min, H_2O_2:NH_4OH:H_2O (1:1:10) for 2 min for the removal of native oxide. Following the chemical cleaning, the wafers were directly loaded into the vacuum deposition chamber, after which metal films were immediately deposited on them. Co/Al multilayer films were fabricated in a cryo-pumped magnetron sputtering system equipped with a rotating table. The base pressure of the deposition chamber prior to the deposition process is about 1×10^{-7} torr. We deposited alternating layers of 15 Å-thick cobalt and 20 Å-thick aluminum on GaAs substrates at room temperature by rotating the substrates directly under DC-powered 2- inch cobalt and aluminum targets. The relative amounts of cobalt and aluminum were controlled by the power applied to the targets. The samples were annealed in a forming gas ambient using an annealing furnace or an RTA system. The RTA system employed was AG Associates Heatpulse 210 system with the ambient gas of flowing forming-gas.

We used TEM to examine the samples for the microstructure analysis. Cross-sectional TEM samples were prepared using the standard TEM sample preparation techniques.[16] We used a Philips EM-430ST microscope operating at 300 kV accelerating potential with a point-to-point resolution of about 0.2 nm. No objective aperture was used for the high resolution microscopy.

For the electrical-property measurements, we made a Schottky diode. To fabricate the Schottky diode, we prepared the cobalt aluminide films in the manner described above, except that the films were deposited on n-type GaAs substrates ($N_d=2\times10^{17}/cm^3$ to $5\times10^{17}/cm^3$). For as-deposited diodes, the ohmic contacts were formed before Co-Al film deposition by Ni/Au/GeNi/Au evaporation, patterning with a lift-off process, and then sintering in an RTA unit at 400°C for 10 seconds in a forming gas atmosphere. For diodes annealed at 600°C and 800°C, the CoAl films were patterned with standard lithography techniques and then etched in a H_2O:HCl (4:1) solution at 60°C. After the deposition of 100 Å Si_3N_4 encapsulant layer by plasma enhanced chemical vapor deposition, samples were annealed in a tube furnace with a forming gas atmosphere at 600°C and 800°C for 30 min. After removal of the Si_3N_4 encapsulant layer in a CF_4:O_2 plasma, the ohmic contacts were formed in the same manner as for the as-deposited samples.

III. Results

Fig. 1 shows a cross-sectional micrograph of an as-deposited multilayer of Co/Al on the GaAs substrate. The alternating layers of Co and Al are uniformly deposited on GaAs without showing interactions between the layers. Co layers appear dark compared to the Al layer in this micrograph. The thicknesses of Co and Al layers are 15 Å and 20 Å, respectively, and total thickness of the final multilayer film is about 700 Å. Upon annealing at 800°C for 30 min, a reaction occurred at the film, and consequently a multilayer in the as-deposited sample was changed to a single-phase film. Fig. 2(a) is the micrograph of the sample after this annealing treatment; it shows that a film with rather large grain (a few μm, laterally) is formed on the GaAs substrate. The interface between the film and the substrate is laterally uniform and no other phase is observed in the film or at the interface between the film and the substrate. In order to identify the film after reaction, we took a microdiffrac-

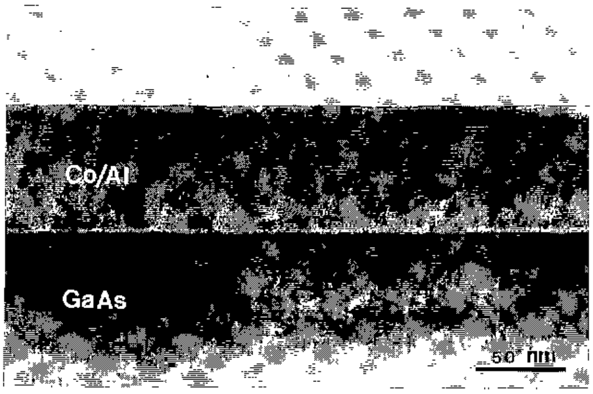

Fig. 1. Cross-sectional TEM image of an as-deposited multilayer of Co/Al on the GaAs substrate. The Co layer appears dark compared to the Al layer in this micrograph.

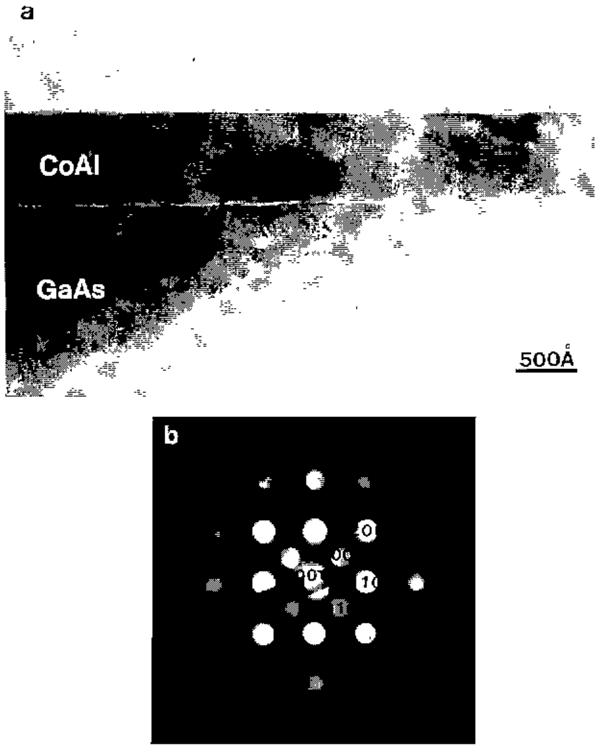

Fig. 2. (a) Cross-sectional TEM micrograph of the multilayer of Co/Al on the GaAs annealed at 800°C for 300 min The micrograph shows that a film with rather large grain (a few m, laterlly) is formed on the GaAs substrate. The microdiffraction pattern from this phase (Figure 2(b) corresponds to (100) of the CoAl phase.

tion pattern from this phase. Fig. 2(b) shows that the diffraction pattern corresponds to that of (100) of the CoAl phase. A high-resolution TEM micrograph taken from this sample also demonstrates that the film is CoAl. Fig. 3 is an HRTEM micrograph taken from the interfacial area between the film and the substrate. The spacing of the high resolution lattice fringes in this micrograph is 2.0 Å, which corresponds to that of the {110} plane (2.02 Å) of CoAl. As shown in the HRTEM micrograph, the interface between CoAl and GaAs is flat and uniform, and does not show any evidence of reaction.

In order to test the electrical characteristics of the CoAl film as a gate electrode for the application to the Self-aligned Gate GaAs MESFET devices, barrier heights of the CoAl-GaAs contact were measured by fabricating the Schottky diode with a CoAl electrode. During the whole processing for the Schottky diode fabrication, the CoAl films remain stable without showing any peeling of the films. Standard I-V measurements were used to obtain the barrier height Φ_B and the ideality factor n of the CoAl/GaAs contact. By plotting the natural logarithm of the current versus the voltage, the barrier height was calculated according to the thermionic emission model.[17] The measured Schottky barrier height of the cobalt aluminide contact is summarized in Table I.

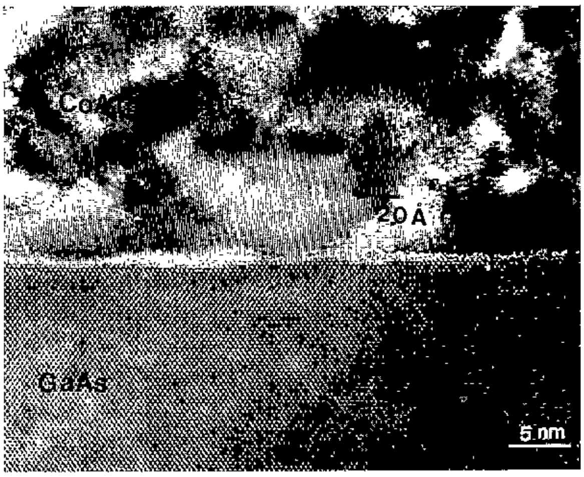

Fig. 3. Cross-sectional HRTEM micrograph of the multilayer of Co/Al on GaAs that was annealed at 800°C for 30 min The spacing of the high resolution lattice fringes in this micrograph is 2.0 Å, which corresponds to that of the {110} plane (2.02 Å) of the CoAl phase. The interface between CoAl and GaAs is flat and uniform, and does not show any evidence of reaction.

Table 1. Schottky Diode Barrier Height B and Ideality Factor n for Increasing Annealing Temperatures for Multilayer-Sputtered Co/Al Films.

	As-deposited	600°C, 30 min	800°C, 30 min
Schottky barrier height Φ_B	0.68	0.68	0.71
Ideality factor n	1.11	1.22	1.35

The data of the as-deposited samples and annealed samples at 600°C show barrier heights of 0.68eV with ideality factor of 1.1 and 1.22 respectively. After 800C annealing, the barrier height is slightly increased to 0.71 with the ideality factor of 1.35.

IV. Discussion

Our results show that the single-phase CoAl film with the grain size of few μm is formed by the deposition of a multilayer of Co/Al film on GaAs and subsequent annealing at 800°C. The CoAl film after annealing shows a uniform and clean interface without any evidence of reaction with the GaAs substrate. These results demonstrate that the CoAl film is thermally stable with the GaAs substrate during the annealing at 800°C for 30 min. Unlike the platinum aluminide formation from a bilayer of Pt/Al,[18] the GaAs below the interface does not show any defects such as stacking faults or precipitates. Therefore, it is demonstrated that the formation of metal-aluminide from a multilayer is a suitable method for high-temperature metallization systems. Our results on the measurements of the barrier heights of the CoAl-

GaAs contacts show that the contact is rectifying after 800°C-annealing process. Also, the measured barrier heights are comparable to the barrier heights measured for refractory metal-nitrides and refractory metal-silicides.[1] Since the annealing at 800°C for 30 min is enough for the self-aligned gate technology, the CoAl film can, therefore, be used as gate electrode materials. It should be noted that the ideality factor of the sample annealed at 800°C is increased to 1.35, which indicates that the diode characteristic deviates from that of ideal thermionic emission model, yet the contacts remain rectifying. Similar degradation of the diodes were observed in NiAl/n-type Schottky diodes.[19] The mechanism for this degradation in the diodes is not clear, and the investigation will require other techniques for the barrier height measurement such as C-V measurement or photoelectric measurements.

IV. Conclusions

We have investigated the formation and thermal stability of cobalt aluminide on GaAs. In order to obtain cobalt aluminide we deposited a multilayer of Co/Al on GaAs, and subsequently annealed the samples at 800°C for 30 min. After the annealing, single-phase cobalt aluminide was produced showing a flat and uniform interface with GaAs, which indicates that cobalt aluminide is thermally stable with GaAs. We have made Schottky diodes and measured the barrier height after annealing at 600°C and 800°C. Although degradation was observed in the samples after 800°C annealing, the diodes were still usable as rectifying gate electrodes. In addition, the adherence and mechanical properties of the as-deposited and annealed Co/Al multilayer structure on GaAs are compatible with those required for device fabrication processes. Therefore, cobalt aluminide can be used as a gate electrode in GaAs metal-semiconductor field-effect transistors.

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