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Low Temperature Formation of Low Resistivity W Contact with Ultra Thin Mixed Layer on Molecular Layer Epitaxially-Grown GaAs

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Abstract. The precursor for the W CVD on GaAs used is $W(CO)_6$. The contact resistance in W/GaAs is obtained by the transmission line measurements of patterned W on heavily doped GaAs grown by MLE. The dependence of the contact resistance on the surface treatment prior to the W CVD is also studied. Barrier height of W/GaAs structure is measured by the temperature dependence of I-V characteristics in reference to the contact resistance. The W/GaAs interface is analyzed using SIMS and RBS. Contact resistance of non-alloyed structure achieved are $3x10^{-7}$ Ωcm^2 for n-type GaAs and below $5x10^{-8}$ Ωcm^2 for p-type respectively. From the physical analyses, the mixed layer in W/GaAs interface is estimated less than 20Å.

1. Introduction

In recent years, the active region of the fast semiconductor devices is localized in atomic scale and the thin layered structure is required with atomic accuracy(AA). In such fast devices, the metal/semiconductor contacts limit net operating speed. In addition, the conventional alloyed contact cannot be applied for such thin layered structures. Therefore, low resistivity metal/semiconductor contact formed at low temperature with thin mixed layer has been urgently required. W/GaAs contacts were found stable up to 500°C. This temperature is higher than used for selective regrowth with the molecular layer epitaxy (MLE) for the 100Å channel GaAs static induction transistor (SIT) [1]. Sputtering was commonly used for W deposition. However, it can result in generation of defects in thin active semiconductor layers.

In this report we present CVD W suitable for ultra-thin devices. The contact resistance in W/GaAs is shown as a function of surface stoichiometry by using the transmission line measurements (TLM) on heavily doped GaAs grown by MLE. Barrier height of W/GaAs is studied in reference to lowering the contact resistance. The W/GaAs interface and the impurity profiles in MLE GaAs layers are measured by secondary ion mass spectrometry (SIMS). Rutherford backscattering spectroscopy (RBS) is used to study the structural properties of W/GaAs interface.

2. Experiments

The precursor for the W deposition on GaAs used is $W(CO)_6$. The W layers were deposited in the MLE reactor [2]. Prior to the W CVD, oxides were removed from GaAs surface, in the deposition chamber, by exposing to AsH_3 below 480°C. Oxides are chemically reduced with this process rather than physically evaporated[3]. Immediately after oxide reduction, $W(CO)_6$ was injected continuously at 360°-400°C with the pressure of 15 mTorr. GaAs surfaces were heated with a halogen lamp located over the wafer.

The contacts to n-type MLE GaAs layers doped with Te on semiinsulating undoped (100) GaAs were studied. The MLE layers were grown with triethylgallium (TEG) and AsH_3 precursors. Diethyltellurium (DETe) was used for doping. P type MLE layers were doped with Zn from diethylzinc (DEZn) or with C from trimethylgallium[4]. W/GaAs contacts were evaluated by a transmission line method (TLM) with the SiN patterned structure. By using SiN remote-plasma

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deposition and two-step etching process, the process-induced defects in W/GaAs interface were safely avoided in TLM fabrication process. Wet etching with $NH_4OH:H_2O_2:H_2O$ was used for patterning of the W layers.

The Schottky barrier heights of W/GaAs contacts were estimated by using temperature dependence of the I-V characteristics. By the following equation, the barrier heights ϕ_b were calculated.

$$Js = A^*T^2\exp(-\phi_b/kT)$$

where Js is the saturation current density, A* is the effective Richardson constant, T is the measurement temperature, k is the Boltzmann constant, V_a is the applied voltage, ϕ_b is the Schottky barrier height.

The impurity profiles in MLE layers were obtained by SIMS. A primary sputtering beam of Cs and O ion with 1keV for negative and positive SIMS were used, respectively. W/GaAs interface profiles were analyzed by time of flight (TOF) SIMS, in which the sputtering beams of Ar^+ of 1keV were used to minimize a mixing effect for high depth resolution.

RBS measurements were carried out by the 1.5MeV He^+ irradiation. W/GaAs samples used for RBS measurements were the same as those for the barrier height measurements. Random spectra were measured by tilting the crystal surface 7° off to the <100> axis. Plane channeling was safely avoided. Angular dependence of the backscattering yield was also measured. He^+ dose for each angular step used was 200nC.

3. Results and Discussion

The deposition could be observed only for pressures higher than 1×10^{-3} Torr, for the entire tested range of temperature 360° - 400°C. Deposition rate was about 3 Å/min on GaAs, like reported for pyrolytic decomposition[5]. However, we can not exclude some photolytic reaction[6]. Although the GaAs substrates were not intentionally illuminated, the light of the halogen heater lamp contained near-UV wavelengths. The W layers on GaAs observed with Nomarski and SEM microscopes appeared mirror-like. The layers on SiN had a grain structure, similar to the one reported previously[5]. The difference in layer morphology between SiN and GaAs suggests a catalytic properties of the GaAs clean surface.

Fig.1 shows the relation of the carrier concentration in MLE layers with Te concentration measured by SIMS. The carrier concentration gradually increased over $1\times10^{19}cm^{-3}$ Te concentration, and beyond $4\times10^{20}cm^{-3}$, decreased rapidly. In this figure, the specific contact resistance ρ_c is also shown as a function of Te concentration. ρ_c strongly depended on Te concentration and had a minimum at the peak of the carrier concentration. For heavily doped semiconductors the tunneling becomes predominant, and ρ_c is determined by the factor, $\exp(\phi_b/N_D^{1/2})$. The dependence was different from the tunneling theory. It can be related to excess Te atoms adjacent to W/GaAs interface. The lowest ρ_c was $3\times10^{-7}\ \Omega cm^2$. This is the lowest reported value for doping concentration in the range of $10^{19}\ cm^{-3}$. Similar values were reported by Patkar, *et al* [7], for molecular beam epitaxial (MBE) GaAs doped with Si as the low temperature grown cap. The MLE layers, reported here, were doped uniformly and no passivation layers were necessary. The fabrication process used was

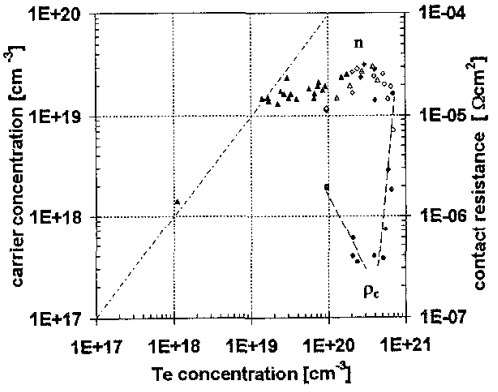

Fig.1 Te concentration dependence of the carrier concentration in MLE layer and the specific contact resistance for W/GaAs

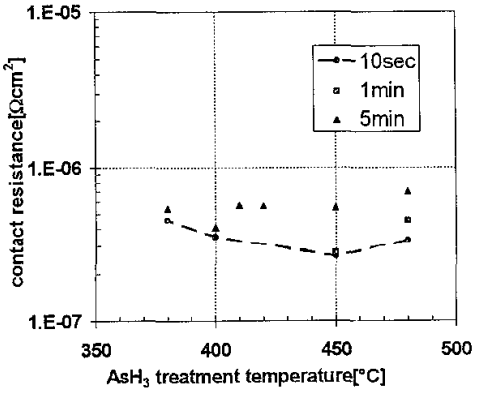

Fig.2 AsH_3 treatment temperature dependence of the specific contact resistance. AsH_3 pressure was 8×10^{-4}Torr.

close to that used for device fabrication, including SiN PE CVD and ozone ashing for semiconductor cleaning. Using uniformly doped top layers of GaAs is advantageous for such an application. In addition, all processes reported here for the CVD W contacts were done at the temperature below 480°C, which is required for ultra-thin devices[1] to prevent their thermal degradation. To achieve ρ_c of 3 - 4×10^{-7} Ωcm^2, it was also necessary to apply AsH_3 treatment temperature below 480°C for oxide reduction prior to the W CVD, as shown in Fig.2. In all experiments, the CVD temperature did not exceed that of AsH_3 treatment. The lowest ρ_c was obtained with the AsH_3 treatment at 450°C 10 s.

The average value of the ρ_c for the W contacts to C-doped p-GaAs was 2×10^{-8} Ωcm^2 at acceptor concentration 3×10^{19} cm^{-3} as shown in Fig.3. The low ρ_c value and low mobility of p-type layers result in large uncertainty of this value. The measured values were from almost 0 to 5×10^{-8} Ωcm^2. At that low ρ_c values, the main source of error was an absolute accuracy of distance measurements between the TLM contacts, which was 0.1 μm in our laboratory. The ρ_c extraction accuracy is lost, if a transfer length $L_t=(\rho_c/R_s)^{1/2}$ becomes comparable to the contact distance measurement accuracy, where R_s is a sheet resistance value. The obtained ρ_c for C dopant was about 1/10 smaller than expected from the hole concentration measured in the MLE layer and literature reports, shown in Fig.3. One possible reason for this is oxide free interface of our layers. The results of Stareev[8], who obtained a low ρ_c value for $N_A=2\times10^{20}$ cm^{-3} after sputter, in-situ, cleaning and annealing, indicate importance of this factor. The ρ_c value for Zn dopant was 10 times larger, 1×10^{-6} Ωcm^2, at the same acceptor concentration average of 3×10^{19} cm^{-3}, than for C. The W contact resistance to the Zn-doped MLE layers corresponds well with the reported ρ_c values(Fig.3). To explain the difference between the W contacts to C-doped and to Zn-doped layers requires further investigation.

Fig.4 shows the dependence of Schottky barrier heights ϕ_b on the surface treatment condition prior to the W deposition. The surface treatment was carried out at 480°C for 30 min under various AsH_3 pressure. W deposition was carried out at 380°C for 30 min. The surface treated without AsH_3, in vacuum 5×10^{-9} Torr, gives the lowest ϕ_b 0.58 eV by I-V characteristics. ϕ_b increases up to 0.8 eV with AsH_3 pressure at 1×10^{-3} Torr. The ideal factor of the Schottky barrier diode on the surface treated without AsH_3 is 1.05, and that with higher AsH_3 pressure, 1.01, indicates that the interface crystal quality depends on the surface treatment prior to the W deposition. From experiments on pin diodes regrown with MLE on AsH_3 treated interfaces, it was also concluded[3], this treatment affects crystal structure in layers adjacent to the interface. This can explain the dependence of the ρ_c value on the treatment temperature though ϕ_b is as high as 0.75 eV. Possible mechanisms include depletion of the surface layers from dopant atoms by their evaporation or exchange reactions, as well as modification of the barrier height by crystal structure changing.

Fig.5 shows the angular dependence of backscattering yield of RBS from the surface W, W/GaAs interfacial region and the bulk region of GaAs. Dip curve was obtained from the W/GaAs SBD mentioned previous paragraph, which W layer is deposited on the GaAs surface heat-treated in vacuum for 30 min just prior to the deposition. As shown in Fig.5, the angular dependence of backscattering yield from the surface W shows clear dip almost at the same angle, where the

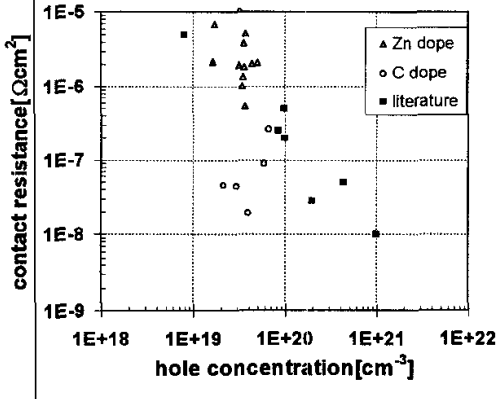

Fig.3 Carrier concentration dependence of the specific contact resistance to p-MLE GaAs

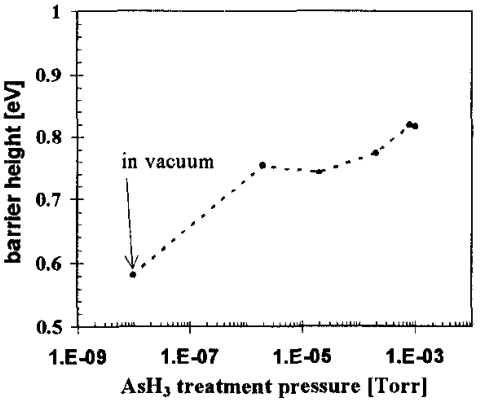

Fig.4 AsH3 pressure dependence of Schottky barrier height in surface treatment. Temperature is 480°C and time is 30min.

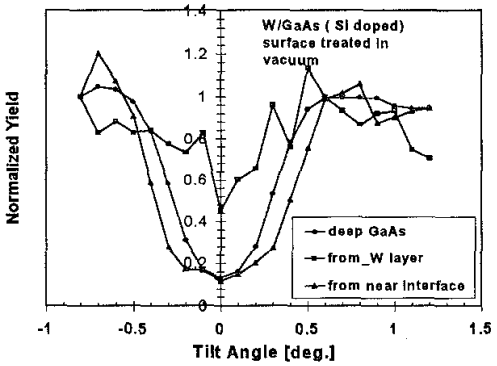

Fig.5 Angular dependence of backscattering yield of RBS from the surface W, the W/GaAs interface and the bulk GaAs

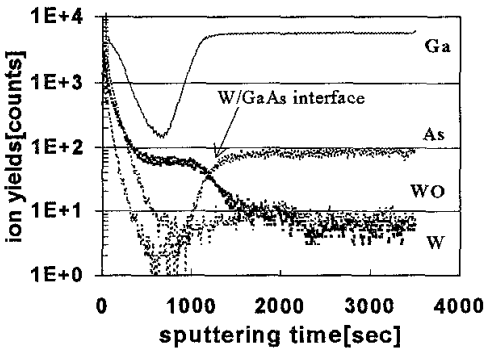

Fig.6 TOF-SIMS profile of W/GaAs. Surface treatment was carried out at 450°C for 10 sec with AsH_3:8×10^{-4}Torr. W was deposited at 380°C for 30min.

underlying GaAs shows <100> axial channeling. Therefore, the W atoms deposited on GaAs show <100> aligned when the GaAs surface is heat-treated in vacuum at 480°C for 30min just prior to the W deposition. As shown previously, the SB height was lowered when the GaAs surface was heat-treated in vacuum at 480°C compared with that heated under AsH_3 exposure of 1×10^{-3} Torr. Whereas the atomic structure of deposited W/GaAs is not clear yet, it is considered that the barrier height of W/GaAs structure is closely related with the atomic alignment of W on GaAs.

In Fig.6, the W/GaAs interface profile measured by TOF-SIMS is shown. W to GaAs interface was clearly separated, and the mixed layer in the interface was estimated less than 20Å. But strange profile was seen on the surface of W. Ga, As and O piled up. And in the W film, O yields reduced, and also C (not shown). It is possible to explain these results by a surface unstability or a matrix effect, but it is necessary to study details further more.

4. Conclusion

In summary, CVD of W from $W(CO)_6$, on MLE n-type layers, doped with Te, gives contact resistance $\rho_c = 3\times10^{-7}$ Ωcm^2 and mirror-like layer morphology. The native oxides can be reduced with AsH_3 prior to the CVD. The AsH_3 treatment and CVD temperatures should not exceed 480°C. The CVD W contacts to p-GaAs MLE layers doped with C give ρ_c in the low range of 10^{-8} Ωcm^2, while for the Zn dopant, only 1×10^{-6} Ωcm^2 was obtained. The low contact resistance is obtained for electrically active dopant concentration about one tenth lower than expected from literature reports. The mixed layer in the interface was estimated less than 20Å. The conditions used for GaAs MLE and W CVD are suitable for self-aligning constructions of ultra-thin devices with regrown epitaxial layers.

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