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Plasma-assisted oxide removal from p-type GaSb for low resistivity ohmic contacts

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The effect of several plasma-assisted oxide removal techniques prior to metallization of p-type GaSb was investigated. Compared to conventional chemical methods, the plasma-assisted oxide removal resulted in significant improvement of the specific contact resistivities, obtained from transfer length method measurements. Very low specific contact resistivities of less than 5×10^{-8} Ω cm^2 were observed after surface pre-treatment by H_2/Ar sputter etching and low-ion-energy argon irradiation. By eliminating sample exposure to air, *in-situ* Ar irradiation becomes a promising technique for high performance GaSb-based semiconductor diode lasers.

I. INTRODUCTION

GaSb-based diode lasers are one of the most promising monochromatic light sources in the mid-infrared wavelength region of 2-5 μm, and low resistance ohmic

contact to GaSb is desirable for high performance operation of these devices. When exposed to air, the GaSb surface quickly forms a 3-5 nm thick surface oxide layer[1]. It is therefore essential to remove this oxide layer prior to metallization to achieve a good ohmic contact.

Current approaches for GaSb native oxide removal are primarily based on wet chemical clean using common acids and bases in semiconductor processing, such as HCl, HF or NH_4OH. Among chemical treatments, HCl clean is reported to be the best choice to create an oxide-free surface[1,2]. However, the chemical treatments prior to metallization lack reproducibility due to the rapid re-oxidation of GaSb. Thus, *in-situ* oxide removal techniques prior to metallization are advantageous. Argon plasma irradiation has recently been used for removal of the native oxide of III-V compounds for contact purposes[3-5] and low-ion-energy Ar^+ irradiation on oxidized GaSb can lead to a nanostructured and oxide-free surface[6,7]. However, the effect on the metal-GaSb contact properties from such Ar^+ irradiation has yet not been fully characterized. Other reported plasma-assisted techniques used to (at least partly) remove the GaSb native oxide are hydrogen (H_2) plasma cleaning and GaSb etching using chlorine-based chemistry[8-10].

In this work, *in-situ* Ar^+ irradiation with different ion energies, H_2 and BCl_3 plasma cleaning were applied to remove the native oxide of p-type GaSb. The effect of each of these oxide removal techniques on the contact properties in comparison with the conventional chemical methods is evaluated via the specific contact resistivity between the metallic layers and p-GaSb.

II. EXPERIMENTAL

2 µm thick epitaxial layers of Be-doped GaSb were grown on n-type GaSb(100) wafers in a Varian GEN II molecular beam epitaxy (MBE) system. The p-type doping concentration was 2×10^{19} cm^{-3} which is a typical concentration for the laser cap layer[11,12]. An n-type GaSb substrate with a nominal carrier concentration of 5×10^{17} cm^{-3} was chosen to create a p-n junction in order to prevent the current leaking into the substrate.

The specific contact resistivity was determined by the transfer length method (TLM) and four-point probe measurements. TLM structures were defined by conventional UV-lithography and were isolated on rectangular mesas by inductively coupled plasma – reactive ion etching (ICP-RIE). Ti/Pt/Au is the standard p-sided metallization for a number of antimonide-based devices. The specific contact resistivity of this metallization is typically in the order of 10^{-7}-10^{-6} Ω cm^2 [5,13]. In this work, the Ti/Pt/Au metallization was performed by e-beam evaporation in a combined sputtering and e-beam evaporation system (AJA ATC-2200V) with Ti-, Pt- and Au-thicknesses of 50 nm, 25 nm and 325 nm, respectively. The different oxide removal techniques applied prior to metallization were:

1- *In-situ* Ar plasma etching with different ion energies (70 eV, 120 eV, 180 eV, 250 eV, and 325 eV) for 1 min at 3 mTorr.

2- H_2/Ar etching by ICP-RIE for 45 s at 80 °C. The baseline etch parameters are 50 W RF power, 400 W ICP power, 50 mTorr chamber pressure, 100 sccm Ar flow rate and 15 sccm H_2 flow rate.

3- BCl_3/Ar etching by ICP-RIE for 1 min at 20 °C. The baseline etch parameters are 15 W RF power, 50 W ICP power, 2 mTorr chamber pressure, 3 sccm Ar flow rate, 10 sccm BCl_3 flow rate and 2 sccm N_2 flow rate.

4- 18.5 % HCl soak for 30 s followed by a deionized water (DIW) rinse for 5 s and quick drying in N_2.

5- 18.5 % HCl soak for 30 s followed by 2 % $(NH_4)_2S$ soak for 5 s and quick drying in N_2.

ICP-RIE was performed in an Oxford plasma system 100 ICP380 reactor. Samples undergoing the surface treatment methods 2 through 5 were immediately transferred to the metallization system (less than 30 s exposure to air). After lift-off, the samples underwent a rapid thermal anneal at 290 °C for 45 s. This annealing procedure is commonly used for contacts to n-type GaSb[14] in laser fabrication, and thus simultaneously applied for contacts to p-type GaSb. Finally, TLM patterns on p-type GaSb epilayer were wire-bonded to the Au bonding pads on glass substrate, as shown in figure 1, for 4-probe measurements using a Lake Shore Hall effect measurement system. The adhesion between the metals and p-type GaSb epilayer was evaluated during the bonding process.

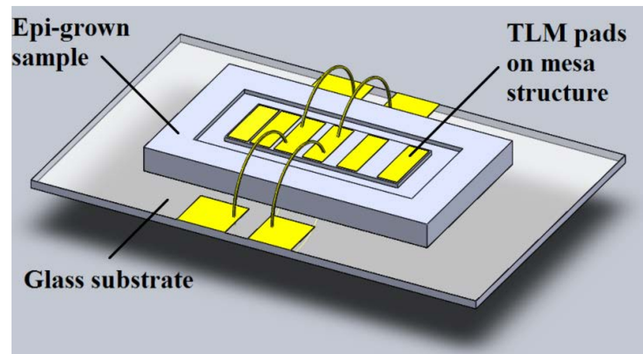

FIG. 1. (Color online) TLM structure wire-bonded to Au pads on glass. TLM pad size is 250 µm x 750 µm and the distance between TLM pads is 25, 50, 100, 175, and 250 µm.

III. RESULTS AND DISCUSSION

The measured specific contact resistivities for different oxide removal techniques are summarized in Table 1.

Table 1: p-type GaSb/Ti/Pt/Au contact: The measured specific contact resistivity and adhesion property for each treatment. Good: the metal contacts after bonding provide excellent electrical connection. Poor: the metal contacts are easily peeled off from the GaSb epilayer during the bonding process. N: number of samples.

Treat-ment	Surface treatment	Lowest ρ_c (10^{-8} Ω cm^2)	Highest ρ_c (10^{-8} Ω cm^2)	Average ρ_c (10^{-8} Ω cm^2)	Adhesion property
1a (N=3)	Ar irradiation - 70 eV	24.1	87.1	47.1 (for N=3)	Poor
1b (N=3)	Ar irradiation - 120 eV	5.42	5.88	5.59 (for N=3)	Good
1c (N=4)	Ar irradiation - 180 eV	0.28	4.28	2.11 (for N=3*)	Good
1d (N=5)	Ar irradiation - 250 eV	2.27	18.8	11.9 (for N=5)	Good
1e (N=3)	Ar irradiation - 325 eV	3.73	17.4	10.5 (for N=3)	Good
2 (N=4)	H_2/Ar etching	---	2.72	2.72 (for N=1*)	Good
3 (N=3)	BCl_3/Ar etching	59.4	65.5	62.4 (for N=3)	Poor
4 (N=3)	HCl soak + DIW rinse	53.2	111	81.7 (for N=3)	Poor
5 (N=3)	HCl soak + sulphur passivation	25.9	32.2	28.4 (for N=3)	Poor

*: Measurement results of the other samples gave negative contact resistance

The TLM only gives accurate/valid results, i.e. consistent with the theory (equations) used, for $\rho_c > 0.2\ \rho_s\ t^2$ where ρ_s is the semiconductor sheet resistance and t is the layer thickness[15], whereas the results are expected to deviate more (in percentage) from theory below this value. In our experiments, $0.2\ \rho_s\ t^2 = 5 \times 10^{-8}\ \Omega\ cm^2$. Thus, the TLM failed to determine accurately the extremely low specific contact resistivities of the contacts after treatment 1c and 2. This is supported by the fact that the measurements of one sample of treatment 1c and three samples of treatment 2 gave a negative contact resistance R_c with the absolute value similar to those of the above results. For each sample, the measurement results were repeatable within 5 percent of the overall mean value, and thus the variation of ρ_c is attributed to the fabrication process.

The results from the conventional chemical treatment, treatment 4, are in line with previously reported results[5]. Comparing the chemical treatments 4 and 5, the sulphur passivation after HCl soak showed the better contact properties. This can be explained by the decrease in the surface state density after sulphur surface treatment[16]. However, the presence of a thin oxide or sulfur passivation layer on the semiconductor surface after these pre-treatments leads to poor adhesion of the metal contacts.

The results of specific contact resistivity from Ar^+ irradiation surface treatment (1 a-e) show the advantage of the *in-situ* oxide removal technique in terms of contact and adhesion properties. At 70 eV, the ion-induced effect was insufficient, resulting in high ρ_c and poor adhesion of the metal contact. When the ion energy was increased, but still moderate, the ion bombardment was adequate to remove the oxide (at least sufficiently to get a good contact) while minimizing the ion-induced damage of the GaSb surface. At 180 eV, the specific contact resistivity to p-type GaSb is lowest and below the limit for

accurate TLM measurement results (i.e. below 5×10^{-8} Ω cm^2). However, at higher ion energies (250 and 325 eV), the ion-induced damage led to the formation of nanodots on the GaSb surface, as depicted in figure 2 and figure 3. The nanodot formation indicates the presence of the Ga rich amorphous layer as has been reported in the literature[17-19] that results in high contact resistances. Hence, as can be seen in figure 4, the best contact is obtained for an optimum compromise between oxide removal and ion-induced damage. The variation in ρ_c for a given ion energy is most likely due to the ion-induced damage of the semiconductor surface and the interface reaction between Ti and GaSb[20]. Note that in this study, the AJA sputtering and evaporation system has low ion density, in the range of 10^7-10^8 ion cm^{-3}. Thus, the estimated projectile Ar^+ fluence was in the range of 10^{13} ion cm^{-2}, which is much lower than the ion fluence threshold of 1×10^{16} ion cm^{-2} for Sb_2O_3 removal and of $> 7 \times 10^{16}$ ion cm^{-2} for Ga_2O_3 removal reported by El-Atwani *et al.*[6,7].

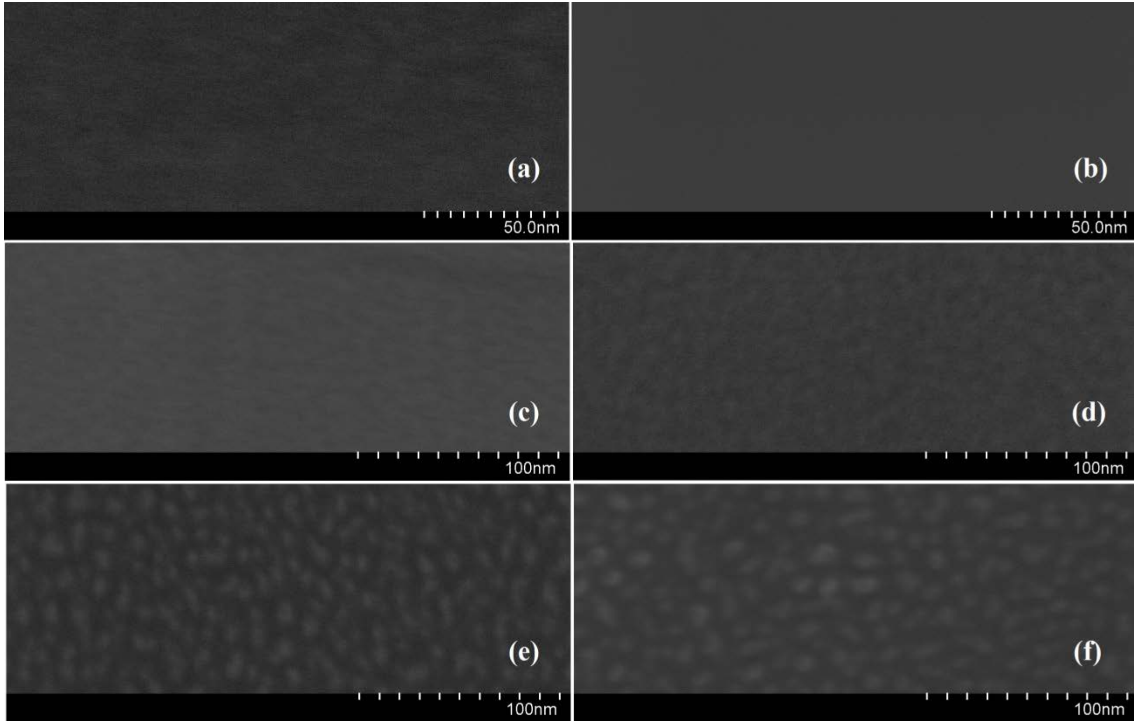

FIG. 2. Scanning electron micrographs of GaSb surface after argon irradiation at (a) non-treatment, (b) 70 eV, (c) 120 eV, (d) 180 eV, (e) 250 eV and (f) 325 eV.

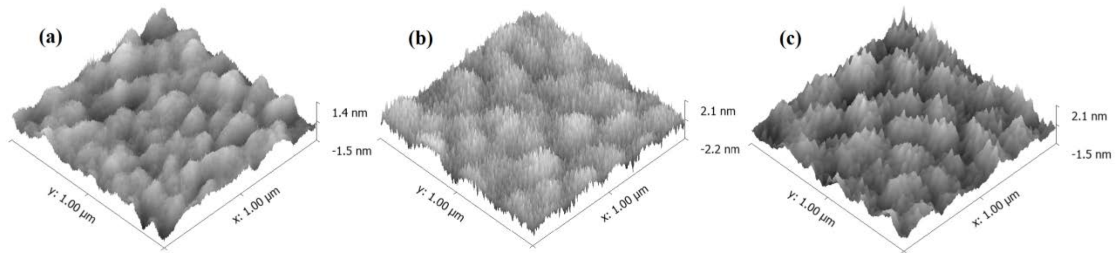

FIG. 3. Atomic force micrographs of GaSb surface after argon irradiation at (a) 180 eV, (b) 250 eV and (c) 325 eV with RMS values of 0.34 nm, 0.52 nm, and 0.44 nm, respectively.

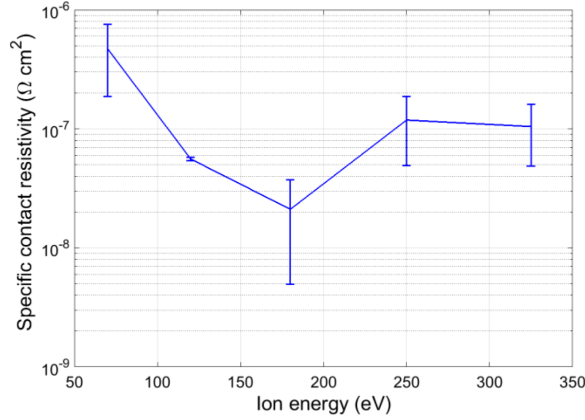

FIG. 4. (Color online) Effect of argon ion energy on the contact properties of p-GaSb via the measurement of specific contact resistivity (average value with the standard deviation shown as error bars). We note that all measured values of the specific contact resistivity for 180 eV ion energy are less than 5×10^{-8} Ω cm^2.

Among plasma-assisted treatment techniques, surface treatment by BCl_3/Ar etching (treatment 3) is non-preferable due to a relatively high contact resistance and poor adhesion. This is most likely due to residual oxide and possibly the presence of chlorine-containing residues after BCl_3 ICP-RIE[21]. As opposed to this, surface treatment by H_2/Ar etching (treatment 2) led to extremely low specific contact resistivity and good adhesion between metallic layers and p-GaSb. We believe this is due to an oxide-free and high quality GaSb surface after the treatment.

IV. SUMMARY AND CONCLUSIONS

In this work, different plasma-assisted techniques were performed prior to metallization to remove the native oxide of epitaxially grown p-GaSb. The effects of these pre-treatment techniques on the electric contact and adhesion properties were compared with that of conventional chemical methods by evaluating the specific contact

resistivities between the metallic layers and p-GaSb. The surface pre-treatment using H_2/Ar etching and low-ion-energy Ar^+ irradiation led to extremely low specific contact resistivities with value below the limit of TLM for accurate value determination. In Ar^+ irradiation surface pre-treatment, optimization of the argon ion energy is required to sufficiently remove GaSb native oxide while minimizing the ion-induced damage of the semiconductor surface. The use of *in-situ* Ar^+ irradiation eliminates sample exposure to the air, thus making it a promising technique for high performance GaSb-based semiconductor devices.

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