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Surface Modification of Sputtered Ga_{.5}In_{.5}Sb Thin Films

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ABSTRACT: Growth of Ga_3In_5Sb thin films was carried out using a in a r.f. magnetron sputtering system on high-purity quartz glasses as a substrate. The target material for the film was grown in the laboratory using Vertical Bridgmen method. The polycrystallinity of the sputtered films were characterized using x-ray diffraction method. The grown films were then treated with Ruthenium (Ru), Platinum (Pt) and Palladium (Pd) ions. XPS studies on the film showed the incorporation of Ru, Pt and Pd along with Ga, In and Sb. However in case of Ru and Pt treated surface a mild oxygen peak was also observed. No such oxide peak was observed in Pd treated surface. SEM studies on the films were also carried out which shows the increase in smoothness of the film after Ru and Pt treatment, whereas the surface deteriorated in case of Pd treatment. This can be interpreted as reduction in surface states induced by passivating oxide formed after Ru and Pt treatment. Electrical characterization of the film viz. Vander Pauw resistivity, Hall mobility etc. measurements also showed improved result compared to untreated and Pd treated surface and is been reported. Finally with chemically treated films Au/Ga₃In₅Sb Schottky diodes were fabricated and electrically characterised for IR detectors. @JASEM

Gallium Indium Antimonide has received attention as a substrate material for fabrication of Ga-AlSb/GaSb IR detectors useful for fiber optic communication. Since the efficiency of detector depends very much on the surface properties of the substrate material, improvement of substrate surfaces is a challenging task in device technology. Reports on the improved electrical properties of GaAs and InP surfaces by Ru³⁺ modification are already available in the literature (Bose, et. al 1984; Heller, et. al 1981; Parkinson, et. al 1979; Rampraksh, et. al 1983). In this communication improved surface properties and enhanced barrier height of Au/n-Ga_{.5}In_{.5}Sb Schottky diodes after Ru³⁺ and Pt⁴⁺ modification of sputtered n-Ga_{.5}In_{.5}Sb polycrystalline substrates are reported.

MATERIALS AND METHODS

Growth of Ga 5 In 5 Sb thin films was carried out using a circular (4 in.-diameter and 0.20 in.-thick) Te-doped polycrystalline n-Ga 5In 5Sb target in a r.f. magnetron sputtering system. The target material for the film was grown in the laboratory using Vertical Bridgmen method (Roy, et.al 1989). The deposition conditions for Ga₅In₅Sb thin films are summarized in Table I. A high-purity quartz substrate with surface roughness less than 0.15µm and a thickness of 0.50 mm was used. After the working chamber was evacuated to 5×10^{-7} torr, high-purity (99.999%) Ar gas was introduced into the chamber. Ga 5In 5Sb input power density was kept at 5.5 W/cm². Looking at the electrical and optical properties, a typical composition of $Ga_x In_{1-x}Sb$ i.e x = 0.5 was chosen for chemical treatment.

The sputtered films were chemically treated with Ruthenium trichloride (RuCl₃); (0.01 molar RuCl₃ in 0.1 molar HCl solution), Potassium Chloroplatinate (K_2PtCl_6); (0.01 molar K_2PtCl_6 in 0.1 molar HCl

solution) and Palladium chloride (0.01 molar PdCl₂ in 0.1 molar HCl solution) for 1 min and then air dried. The optical Band gap was determined by the optical absorption method using a Shimadzu double monochromator recording spectrophotometer (model UV-365). The resistivity (ρ) was measured by the four probe point method using the Vander Pauw technique. The Ohmic contact was made by use of a thermally evaporated indium film followed annealing at 150° C for 2 minutes in H₂ atmosphere. The mobility (μ) and carrier concentration (N_D) were determined by Hall-Effect experiment. The Schottky diode was fabricated by thermally evaporating gold. I-V and C-V characteristics were studied using the Keithley 177 microvolt digital multimeter and Boonton C-meter (1MHz). SEM photographs were taken using Camscan series 2DV scanning electron microscope. ESCA results were obtained from ESCA LAB-MK II spectrometer. All the experiments were conducted at room temperature.

RESULTS AND DISCUSSION

The optical band gap (direct) of the sputtered films was found to be 0.44eV at room temperature for both untreated and chemically treated (Ru³⁺, Pt⁺⁴ and Pd) samples. While the carrier concentration (N_D) remained almost the same for both the modified and unmodified samples (~3 x 10¹⁹cm⁻³), the resistivity decreased from 4.6 ×10⁻⁴ to 3.2 ×10⁻⁴ and 3.8 ×10⁻⁴Ω- cm for Ru and Pt treated samples. In case of Pd treated samples the resistivity increased to 7 x 10⁻⁴Ω- cm. While the mobility increased from 350 to 620 and 525 cm²/V-s after Ru and Pt modification, the mobility deteriorated to 275 cm²/V-s after Pd treatment.

Table 1. Deposition conditions of Ga_{.5}In_{.5}Sb thin films

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Conditions	
Target	Ga _{.5} In _{.5} Sb (4 in dia).
Power density	5.5 W/cm ²
Base pressure	5×10^{-7} Torr
Working pressure	5.5 mTorr
Substrate	SiO ₂ , 0.50 mm (t)
Substrate	23 °C
temperature	

Table II summarizes the result. From the I-V and J-V characteristics for Au/n-Ga_5In_5Sb Schottky diodes, the dark current density (J₀) was found to decrease from 3.7 ×10⁻⁴ to 2.3 ×10⁻⁴ A/cm² (for Ru) and 3.25 ×10⁻⁴ A/cm² (for Pt) treated samples. The ideality factor (n) reduced from 3.0 to 2.0 and 2.7 after Ru and Pt treatment. Thus except Pd treatment Ru³⁺ and

 Pt^{+4} shows an improvement in the diode characteristics after modification. C-V measurements were taken at 1MHz frequency at room temperature. Barrier height (V_{bi}) was determined from the C⁻²-V plot and an increase from 0.50 to 0.63eV and 0.60eV was obtained after Ru and Pt treatment and as usual barrier height decreased after Pd modification. SEM pictures (fig.1) shows etch pits in the untreated samples and the featureless smooth surface after Ru³⁺ and Pt⁴⁺ treatment. An ESCA (fig.2) study confirmed the incorporation of ruthenium and platinum on the sputtered Ga₅In₅Sb surface. The experiments were also repeated with Pd treated surface, but no improvement was observed. In fact the diode characteristics of Pd treated films deteriorated compared to untreated one.

Table 2. Electrical properties of Untreated and treated Ga _{.5}	In _{.5} 8	;S	5
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	Untreated	Ru treated	Pt treated	Pd treated
	Ga_5In_5Sb	Ga.5In.5Sb	Ga.5In.5Sb	Ga_5In_5Sb
$\rho(\Omega-cm)$	4.6 x 10 ⁻⁴	3.2×10^{-4}	3.8 x 10 ⁻⁴	7 x 10 ⁻⁴
$\mu(cm^2/V s)$	350	620	525	275
$N_{\rm D}(\rm cm^{-3})$	3.04 x 10 ¹⁹	$3.14 \ge 10^{19}$	$3.00 \ge 10^{19}$	3.12 x 10 ¹⁹
V _{bi} (eV)	0.50	0.63	0.60	0.42
$J_o(A/cm^2)$	3.7 x 10 ⁻⁴	2.3 x 10 ⁻⁴	3.25 x 10 ⁻⁴	5.6 x 10 ⁻⁴
n(ideality	3.0	2.0	2.7	4.2
factor)				

The increase in mobility from 350 to 620 and 525 $\rm cm^2/V$ is possibly due to the grain boundary passivation of sputtered polycrystalline n- Ga_{.5}In_{.5}Sb after the Ru³⁺ and Pt⁴⁺ treatment. Similar results were also reported by Barman et. al.(1990) and Mandal, et. al.(1986) for polycrystalline GaSb and CdTe respectively. The I-V characteristics of Au/n-Ga_{.5}In_{.5}Sb Schottky diodes show improvement in their rectifying behavior and a reduction in the reverse saturation current.



Fig.1a. SEM micrograph of Untreated n- Ga_{.5}In_{.5}Sb



Fig.1b. SEM micrograph of Ru $^{3+}$ treated n-Ga₅In₅Sb

This improvement may be attributed to the reduction of interface states after the Ru³⁺ and Pt⁴⁺ treatment. A similar improvement was also obtained by Parkinson, et. al.(1979) for n-GaAs electrolyte interface and Bose, et al.(1984) for Ag/n-InP Schottky diodes respectively. In this investigation as shown in Table-II, the decrease of both the ideality factor, n, and dark

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current density, J_0 , as obtained from the lnJ-V plot after the Ru³⁺ and Pt⁴⁺ treatment are most likely due to the passivation of the interface states of the junction. This is further supported by the increase in barrier



Fig.1c. SEM micrograph of Pt $^{4+}$ treated n- Ga₅In₅Sb

height from the C⁻²-V characteristics. The improved surface properties according to Parkinson, et al.(1979) is due to the strong adsorption of Ru^{3+} and Pt^{4+} ion followed by splitting and partial removal of the

surface states from the band gap due to the electrostatic interaction. Similar behavior was also reported by Ramprakash, et. al.(1983) and Barman, et. al.(1990) for n-InP and GaSb respectively after Ru³⁺ modification. Incorporation of Ru³⁺ and Pt⁴⁺on n-Ga_xIn_{1-x}Sb surfaces was confirmed by ESCA which shows a distinct peak for ruthenium and platinum Similar Pd peaks were also seen through ESCA analysis. The deterioration in Pd treated samples might be due to adsorption of hydrogen on the surface. Thus Pd acts as reducing agent resulting to activating surface states at the grain boundaries of n-Ga_xIn_{1-x}Sb surfaces and thus deteriorating the electrical properties of Au/n-GaxIn_{1-x}Sb Schottky diodes. SEM photographs (figs. 1a, 1b & 1c) clearly show the removal of surface defects and formation of a featureless surface after Ru and Pt modification.

Conclusion: The surface properties of sputtered polycrystalline n- $Ga_{.5}In_{.5}Sb$ surfaces could be appreciably improved by chemical treatment with Ru^{3+} and Pt^{4+} ions due to the removal of defect states from the band gap region. The Schottky barrier heights are also increased after Ru^{3+} and Pt^{4+} treatment.



Fig.2. XPS spectra of (a) untreated, (b) Pt^{4+} treated and (c) Ru^{3+} treated n- Ga₅In₅Sb.

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