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Schottky Contacts on n-InP with High Barrier Heights and Reduced Fermi-Level Pinning by a Novel Electrochemical Process

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Schottky contacts with nearly ideal thermionic emission characteristics on n-InP were fabricated by a novel *in situ* electrochemical process. The novel electrochemical process reduces Fermi-level pinning. The Schottky barrier height was found to change over a wide range(from 0.35 to 0.86eV), depending on the workfunction of the contact metals. The Pt/InP contact gave the highest barrier height of 0.86eV. The results of atomic force microscopy(AFM) and XPS measurements indicate that the novel electrochemical process produces a smooth and oxidefree interface.

1.INTRODUCTION

Schottky contacts on n-InP have potentially wide applications in semiconductor electronics because InP has higher electron peak velocity and saturation velocity, higher breakdown field and higher thermal conductivity compared to GaAs. However, the InP Schottky barriers has produced only low barrier heights of about 0.4eV due to the firm interfacical Fermi-level pinning¹). This has been an obstacle to formation of practically useful InP Schottky contacts.

The purpose of this paper is to demonstrate that a wide range(from low to high) of Schottky barrier height(SBH) can be realized on InP substrates by using our novel *in situ* electrochemical process, reported for GaAs last year²). This process produces nearly ideal Schottky contacts on n-InP with reduced Fermi-level pining, enabling one to obtain various barrier heights by selecting contact metals. The process consists of controlled anodic etching of InP and subsequent cathodic deposition of metal, both of which were done in situ in the same electrolyte. The electrolyte contains barrier metal ions and is based on chloric or sulfuric acid. Etching is done by anodic dissolution. Control of etching depth is achieved through control of amount of holes required for anodic oxidation by application of electric avalanche pulses²⁻⁴⁾. The InP Schottky contacts with various metals(Ag, Sn, Cu, Co, Pd, Ni and Pt) have been formed by using different electrolytes. SBH values range from 0.35eV to 0.86eV could be obtained by this process.

2.EXPERIMENTAL

N-type InP crystals with a donor density of $5x10^{15}$ cm⁻³ and (100) orientation were used as substrates. A Ge-Au-Ni contact layer was deposited on backside of the substrates at room temperature and annealed in H_2 at 350°C for 5 minutes to form ohmic contact. The front InP surface was masked by photoresist to define the diode circles. The novel electrochemical process was performed in a three-electrode electro-



Fig. 1 Experimental set-up of the electrochemical process and pulse forms for the etching and plating.

chemical cell shown in Fig.1(a), which has a saturated calomel electrode (SCE) as a reference electrode and a Pt counterelectrode. The InP substrates were fixed with wax to sample holder and connected electrically to the outer circuit by a spring. Figure 1(b) shows the electric pulse waveforms for avalanche pulse–etching and pulse–plating, respectively. After one hundred nanometer thick InP was etched, Schottky barrier was immediately formed by *in situ* pulse–plating of metal on InP. Seven kinds of electrolytic solutions, based on chloric or sulfuric acid and contained metal ion chemicals, i.e., AgCl, SnSO₄, CuCl₂, CoSO₄, PdCl₂, NiSO₄+NiCl₂ and H₂PtCl₆, were prepared for depositing Ag, Sn, Cu, Co, Pd, Ni and Pt, respectively.

For purpose of comparison, Ag, Cu, Al, Pd, Ni and Pt/InP Schottky contacts were also formed by conventional vacuum evaporation techniques on chemically etched InP surfaces. Prior to vacuum evaporation, InP surface was chemically etched in a solution of $H_2SO_4:H_2O_2:H_2O=3:1:1$ with subsequent oxide removal in HF-based solution.

The structural and electrical properties of the Schottky contacts on InP produced by the novel process were characterized as compared with the vacuum evaporated contacts, by using atomic force microscopy(AFM), X-ray photoemission spectroscopy(XPS), current-vol-tage(I-V), capacitance-voltage(C-V) techniques.

3.RESULTS AND DISCUSSION

Roughness of the etched surfaces prior to metal deposition was investigated by AFM. Figure 2 shows a typical AFM image of the etched surfaces after removal of 100nm of InP surface layers by the avalanche-pulse electrochemical etching. The surfaces was smooth with the rms roughness of 0.5nm. No holes due to local avalanche breakdown were observed on the etched surfaces. On the other hand, the rms roughness of the chemically etched surfaces was 1.1nm, being larger than that of the electrochemically etched surface. The results indicate that the electrochemical process results in a smoother surface.



Fig. 2 AFM image of the InP surface obtained by the avalanche pulse electrochemical etching.



Fig. 3 XPS spectra of $In3d_{5/3}$ and P2p core levels from the Pt/InP Schottky interfaces formed by (a)electron beam deposition and (b) novel electrochemical process.

The chemical properties of the Schottky interfaces were investigated by XPS, after revealing the interface region by Ar^+ ion sputtering. Figure 3 shows the observed typical XPS spectra of the surface-sensitive In3d_{5/2} and P2p core levels at the Pt/InP interfaces formed by various processes. The interfaces prepared by the novel electrochemical process was almost free of oxide, whereas that by the vacuum evaporation showed the signals of P oxide and In oxide. This indicates that the novel electrochemical process prevents oxide formation as in the case of GaAs².

The typical I-V characteristics of the Schottky con-



Fig. 4 The forward I–V characteristics of the metal/InP Schottky diodes fabricated by the novel electrochemical process

tacts formed by the novel electrochemical process are shown in Figure 4. The I–V data were analyzed in term of the thermionic emission model of current⁵⁾. The value of the effective Richardson constant was 9.4Acm⁻². Except for Ni, the Schottky contacts showed nearly ideal thermionic emission characteristics of ideality factors close to unity. The Pt/InP contact gave the highest barrier height of 0.86 eV, very close to that determined by C–V measurement. This is the highest SBH ever reported for n–type InP Schottky barrier contact by simple metal deposition. Furthermore, SBH showed clear and systematic dependence on the metal workfunction.

On the other hand, as shown in Figure 5, the Schottky contacts formed by the vacuum evaporation showed



Fig. 5 The forward I–V characteristics of the metal/InP Schottky diodes fabricated by the vacuum evaporation process



Fig. 6 Metal Work function dependence of Schottky barrier height of metal/InP contacts formed by the novel process and the vacuum evaporation.

low barrier heights in the range of 0.37–0.46eV with no clear dependence on the metal workfunction, though they showed reasonably good thermionic emission characteristics except for Pt.

The measured dependence of the Schottky barrier height on the currently accepted values of the metal workfunction are plotted and compared in Figure 5. It is evident that in contrast to the firm Fermi-level pinning observed for the GaAs electrochemical Schottky contacts1), the SBH values of the InP electrochemical Schottky contacts is strongly dependent on the metal workfunction, giving $S(= d\phi_{Bn}/d\phi_m)$ of the interface index of about 0.4. On the other hand, the vacuum evaporation processes resulted in the Fermi level pinning at the InP Schottky contact interfaces. The difference of behavior between the electrochemical and vacuum deposited InP Schottky contacts and that between the electrochemical InP an GaAs Schottky contacts can be explained at least qualitatively in terms of the relationship between the energy involved in the processing and the energy of cohesion at the semiconductor surface.

4.CONCLUSIONS

Schottky contacts with nearly ideal thermionic emission characteristics on n-InP were produced by a novel *in situ* electrochemical process and characterized by AFM, XPS, I-V and C-V techniques. In contrast to the conventional vacuum evaporation, the novel electrochemical process produces a smooth and oxide-free Schottky contact interfaces. The SBH of the InP electrochemical Schottky contacts can be changed over a wide range(from 0.35 to 0.86eV) depending on the workfunction of the contact metal. The Pt/InP gave the highest barrier height of 0.86eV.

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