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Formation of Oxide-Free Nearly Ideal Pt/GaAs Schottky Barriers by a Novel *In-Situ* Photo-Pulse-Assisted Electrochemical Process

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An oxide–free nearly ideal Pt/GaAs Schottky barrier was fabricated by a novel *in–situ* photo–pulse–assisted electrochemical process. The very good electrical characteristics of a high barrier height ϕ_{Bn} of 1.07eV and an ideality factor of n=1.05, were obtained. The results of atomic force microscopy(AFM), XPS and DLTS measurements indicated that the novel electrochemical process produces a smooth and oxide free interface and prevents formation of process–induced damage. It produces a firm Fermi level pinning which was previously possible only by UHV processes.

1. INTRODUCTION

Refractory metal Schottky barrier diodes find many application in advanced semiconductor electronics because of inherent high stability of the barrier metal. However electron beam(EB) deposition which is the standard technique for their preparation induces significant amount of process–induced defects into the surface region, as we have recently shown[1)].

The purpose of the paper is to demonstrate that an oxide–free nearly ideal Pt/GaAs Schottky barrier with good electrical characteristics can be fabricated by a novel *in–situ* photo–pulse–assisted electrochemical process. It is a low–cost, soft, low damage and highly controllable process. The novel electrochemical process consists of controlled anodic etching of GaAs surface and subsequent cathodic deposition of Pt metal, both of which are done *in–situ* in the same Pt solution based on chloric acid. Etching was done by anodic oxidation followed by dissolution. Control of etching depth was achieved through control of amount of holes required for anodic oxidation[2)] by a novel method of supply of photo–pulses in contrast to the previous approaches.[3,4)] In order to investigate the dependence of the barrier height on metal work function, other metals, such as Ag and Cu, were deposited by the same electrochemical process with different electrolytic solutions.

For the purpose of comparison, Pt/GaAs barriers were formed also by an *in–situ* electric avalanche–pulse–assisted electrochemical process[4,5)] and by the standard EB deposition on chemically etched surfaces.

2. EXPERIMENTAL

N–type GaAs crystals with a donor density of $2 \times 10^{16} cm^{-3}$ and (100) orientation were used as substrates. Ge–Au was deposited on the backside of the substrate to form an ohmic contact. The front GaAs surface was masked by photoresist to define the diode

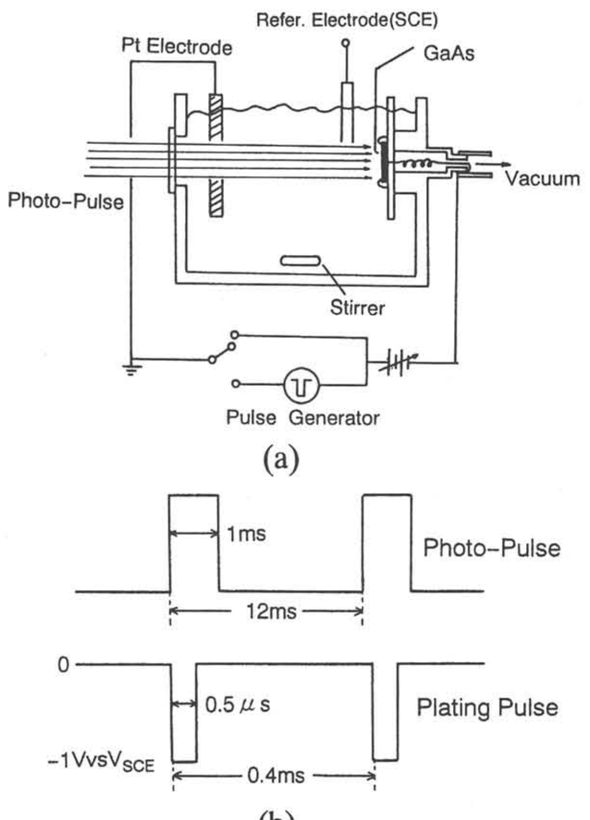

Fig. 1 (a)Experimental setup of the *in–situ* electrochemical processes and (b) photo–pulse and electric plating waveform for plating–pulse.

circles. The novel *in-situ* photo-pulse-assisted electrochemical process was performed in a three-electrode electrochemical cell with a saturated calomel electrode as a reference electrode and a Pt counterelectrode, as shown in Fig. 1(a). Figure 1(b) gives the photo-pulse waveform produced by chopped tungsten lamp and the electric pulse waveform for pulse-plating. After one hundred nanometers of GaAs were etched by anodic oxidation and subsequent dissolution, Schottky barrier was immediately formed by *in-situ* pulse-plating of Pt metal on GaAs. Three kinds of electrolytic solutions, i.e., 1MHCl(200ml)+H_2PtCl_6(1g), 1MHCl(200ml)+AgCl(1g) and 1MHCl(200ml)+$CuCl_2$(1g) were prepared for depositing Pt, Ag and Cu, respectively. In the same electrochemical system Pt/GaAs Schottky diode was formed also by the *in-situ* avalanche-pulse-assisted electrochemical process, where holes were supplied by avalanche voltage pulses with 25V amplitude. Prior to standard EB deposition of Pt in vacuum, GaAs was chemically etched in a solution of H_2SO_4:H_2O_2:H_2O=3:1:1 with subsequent oxide removal in a HCl:H_2O=1:1 solution.

The Schottky barrier diodes were characterized by current-voltage(I-V), capacitance-voltage(C-V), atomic force microscope (AFM), x-ray photoemission spectroscopy(XPS) and deep level transient spectroscopy(DLTS) techniques.

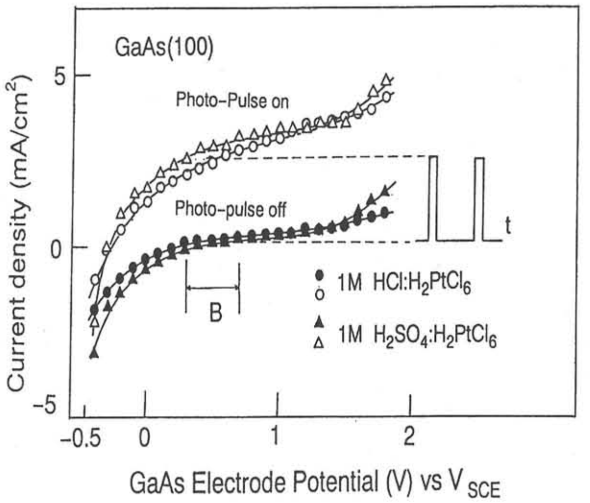

Fig. 2 The current-potential(I-V) curves of n-GaAs(100) electrodes under the illumination by the photo-pulse.

3. RESULTS AND DISCUSSION

The current density of the GaAs electrodes was measured as a function of the electrode potential. Figure 2 shows the I-V curves under the illumination by photo-pulses. The current showed a saturated region where the anodic current is kept to a very small value in the dark. It was increased by light excitation and the anodization took place. By limiting the anodic potential in the region B of Fig. 2, the new photo-pulse-assisted electrochemical process allows precise control of etching of 0.003nm/pulse.

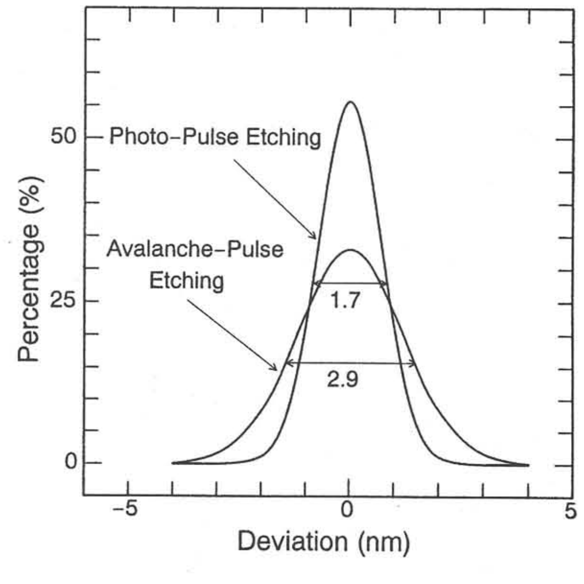

Fig. 3 The histograms of the deviations from the mean height on the etched surfaces, determined by atomic force microscope(AFM).

Reflecting spatially more uniform nature at photo-supply of holes than the avalanche supply, AFM study demonstrated that surface roughness was much reduced. Figure 3 shows the histograms of the measured deviations from the mean height on the etched surface, giving rms roughness of 0.7nm for the photo-pulse etching and 1.2nm for the avalanche-pulse etching, respectively. The results indicate that the photo-pulse etching process can avoid the local breakdown of the

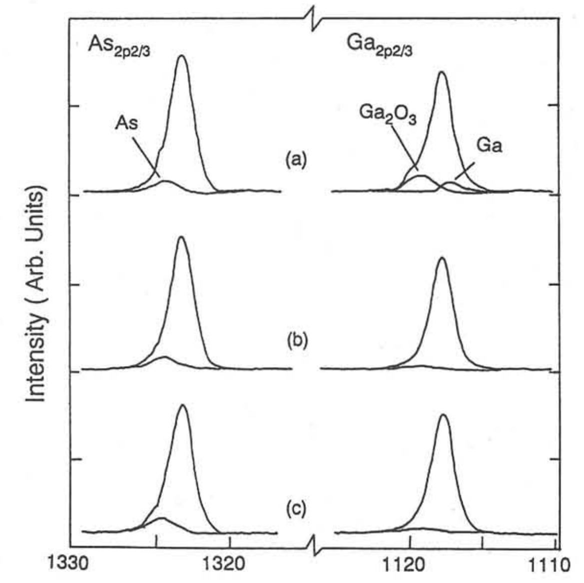

Fig. 4 XPS spectra at the Pt/GaAs interfaces formed by:(a)EB deposition, (b)the pulse-etching electrochemical process and (c)the photo-pulse electrochemical process.

surface voltage barrier in the avalanche-pulse etching, and results in a better surface quality.

Figure 4 shows XPS spectra at the Pt/GaAs interfaces formed by various techniques. The metal-semiconductor interfaces prepared by the *in-situ* electrochemical processes were free of oxide and elemental Ga, whereas those by EB deposition showed the signals of Ga oxide and elemental Ga. Since the electrochemical process is a low energy process it does not decompose GaAs. Furthermore *in-situ* etching and deposition prevents oxide formation.

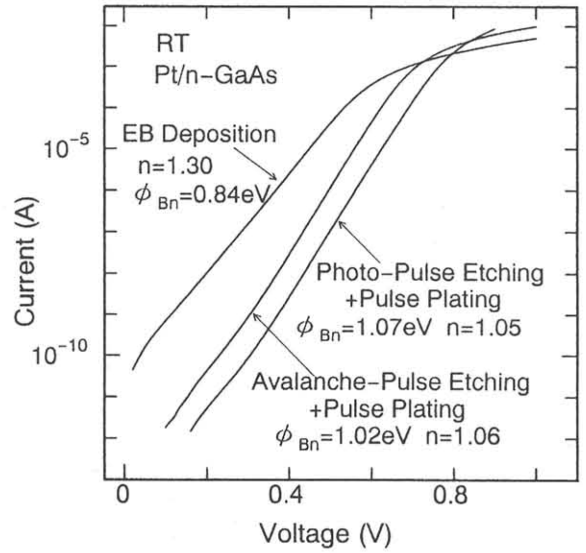

Fig. 5 Forward current-voltage(I-V) characteristics of Pt/GaAs Schottky diodes fabricated by the three kinds of process.

Typical forward I-V characteristics of Schottky diodes with area of $2.3x10^{-3}cm^2$ are shown in Fig. 5. The novel electrochemical diodes gave excellent characteristics with the best results of a Schottky barrier height $\phi_{Bn}{}^{I-V}$ of 1.07eV and an ideality factor of n=1.05. C-V measurements gave a $\phi_{Bn}{}^{C-V}$ value of 1.09eV. The results indicate that a well-behaved and well-controlled Pt/GaAs interfaces can be obtained by the novel electrochemical process. On the other hand, EB technique gave poor characteristics with a larger ideality factor n of 1.3 and $\phi_{Bn}{}^{I-V}$ of o.84eV.

Figure 6 shows the measured dependence of Schottky barrier height on the metal work function. ϕ_{Bn} is independent of the metal function, indicating presence of firm Fermi level pinning. This is characteristics of oxide-free intimate contacts to GaAs previously obtained only by depositing metals to cleaved surface or MBE clean surface in UHV environments[6].

DLTS studies of the electrochemically processed diodes detected no considerable deep levels, which is similar to the Al/GaAs Schottky diodes fabricated by *in-situ* MBE process[1]. This is consistent with the inherently gentle nature of the electrochemical process which prevents formation of process-induced damages in contrast to the EB deposition process with higher energy.

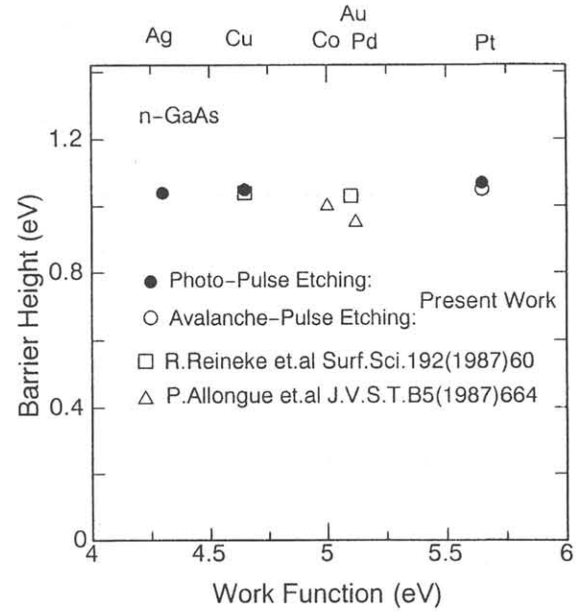

Fig. 6 Schottky barrier height of metal/GaAs contactsby electrochemical processes. The barrier height were determined from I-V measurement, taking account of image force correction of +0.04eV.

4. CONCLUSION

Oxide-free nearly ideal Schottky barriers of Ag, Cu, Pt/GaAs were produced by a novel *in-situ* photo-pulse-assisted electrochemical process and characterized AFM, XPS and DLTS techniques. N-type Schottky barriers exhibit excellent electrical characteristics with n close to unity and barrier heights higher than 1eV. Metal workfunction dependence of barrier heights were similar to those obtained under UHV conditions.

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