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Growth of GaAs Oxide Layer Using Photoelectrochemical Method

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Recently, the conventional silicon-based metal-oxide-semiconductor field effect transistors (MOSFETs) have enjoyed a tremendous success in the IC industry. Their performances can be further enhanced, of course, if the silicon-based MOSFETs are replaced with compound semiconductors. III-V based MOSFETs would operate with a higher speed, a lower leakage current, a higher breakdown voltage, and a higher working temperature capability. These attractive features have motivated many researchers to investigate the potentials and performance characteristics of III-V-based MOSFETs. However, unlike silicon, it is difficult to directly grow the oxide layer with an acceptable quality on the III-V compound semiconductors. The quality of the device is limited by the interface contaminants between external deposited oxide and GaAs, which inherently exist on the surface of the GaAs wafer before insulator layer deposition. Exploiting new oxidation methods to avoid these possible disadvantages are obviously of interests. The wet photoelectrochemical (PEC) etching method is a typical example of this kind, although it is usually used to etch III-V semiconductor. In this work, we were trying to use the PEC oxidation method to grow an oxide layer on the GaAs surface directly. The parameters of the PEC method for forming GaAs oxide layer were experimentally examined. The chemical composition, the atomic bonding and the structure of the resulted surface layers were measured. The results confirmed the layers to be the required oxides. The influence of the thermal treatment to the oxide layer was also studied. The general mechanism of the PEC method has been well understood [1]. Consider a PEC system composed of an n-type GaAs immersed in an electrolyte solution. The band diagram of the n-GaAs/electrolyte interface resembles the band diagram of the Schottky contact. When above-bandgap photons are absorbed at the surface layer of the GaAs sample, electron-hole pairs are created. The built-in electric field in the surface space-charge region will drive holes to the semiconductor/electrolyte interface and electrons to the interior of the n-type GaAs. Because of the existence of holes at the liquid-solid interface, GaAs will be oxidized via the following half reactions [2]:

$$GaAs+6h^{+} \rightarrow Ga^{3+}+As^{3+} \qquad (1)$$

where h^{+} indicates the holes.

In the PEC oxidation system, a He-Ne laser with a wavelength of 632.8 nm is used as the light source, which is compatible with the smaller bandgap of the sample n-type GaAs used in the study. The laser beam is expanded and then reflected onto the sample dipped in a bath of the electrolytic solution. The pH value of the solution is monitored with a pH meter. An amperometer is connected between two Pt electrodes, of which one is contacted with the metal mask on the sample and the other is just immersed in the solution. The sample surface other than the central circular area was covered with a AuGeNi/Au metal mask for electric contact with the Pt electrode. The diluted HCl or NH_4OH were used as the electrolytic solution, of which the pH value was adjusted by varying the concentration. During the PEC process the GaAs samples dipped in the solution were illuminated with a He-Ne laser of an intensity of 6.8 mW/cm^2 for 30min to induce the PEC reaction on the GaAs surface.

Figure 1 shows the oxide growth rate and dissolution rate, averaged over 30 min, as a function of the pH value of the electrolytic solution. The experimental results show when the pH value is between 4.5 and 8.5, i.e. the solution is weak acidic or alkaline, nearly no PEC reaction can be observed. When the pH value is below 3 or above 9 the etching (oxide dissolution) rate is much larger than the growth rate. Only when the pH values lies in a narrow region around 3.5 the growth rate is larger than the etching (dissolution) rate. In other words, the pH value of 3.5 is the only suitable condition to be used to directly grow the oxide layer on GaAs surface. Figure 2 shows that the thickness of the resulted layer grown on the GaAs surface under that condition varies with the PEC treatment time. As shown in Fig. 2, the layer thickness increases but the growth rate decreases with the oxidation time. This kind of time dependence can be understood considering the fact that the electrolytic solution was more difficult to permeate through the previously formed oxide layer to react with the generated holes. Figure 3 shows the thicknesses of the oxide layers as a function of the thermal treatment time at different temperature. It can be seen that in all the cases the thickness of the GaAs oxide film decreases with both the annealing temperature and the annealing time. Moreover, the thickness of the oxide layer decreases rapidly within the first 10 min of the treatment and then tends to a stabilized value for the treatment time above 30 min. This phenomenon indicates that the as-grown GaAs oxide film has a lower density and become a denser oxide film by thermal treating process. The elements ratio of O/(Ga+As) in the surface layer derived from the AES data were 1.39, 1.43, 1.51 and 1.52 for the as-grown GaAs oxide and the oxides annealed at 200, 300 and 400℃ for 30 min in O_2 ambience, respectively. It is evident that the ratio is very close to the value for Ga_2O_3 and/or As_2O_3, especially for the annealed sample. In order to get further information about the bonding structure the XPS spectra of the core-level Ga3d and As3d of the GaAs oxide films were analyzed. Figures 4(a) shows the XPS spectra of Ga3d, from which it can be seen that for the as-grown sample the Ga3d spectrum is composed of two bands located at 21 eV and 19.4 eV, corresponding to Ga_2O_3 and GaAs, respectively. But for samples annealed in O_2 ambient at temperatures 200, 300 and 400℃ only the Ga_2O_3 signal exists in the spectra. Similarly, as shown in Fig. 4(b), the spectrum of As3d of as-grown sample contains two bands at 44.9 eV and 41 eV, which correspond

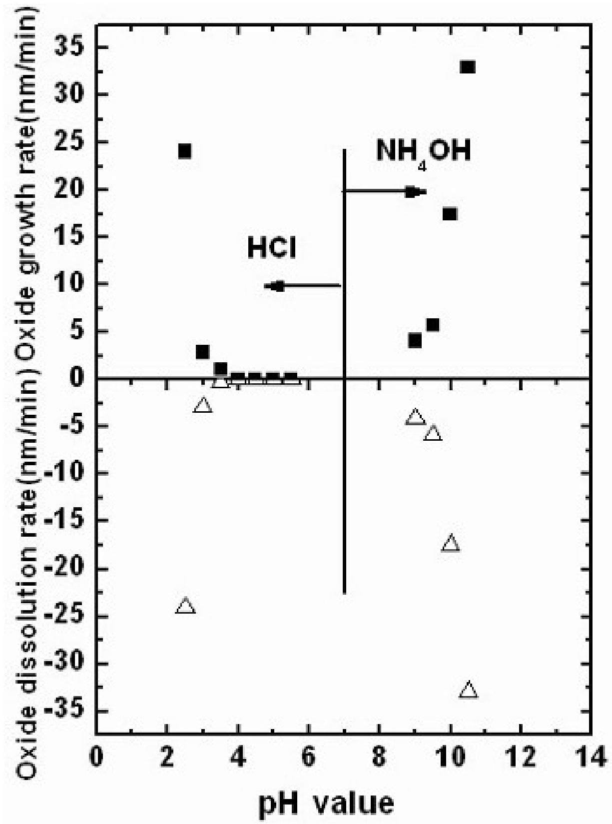

Fig. 1 The oxide growth rate and dissolution rate as a function of the pH value of the electrolytic solution. The PEC treatment time is 30 min.

to As_2O_3 and GaAs, respectively, but only the As_2O_3 signal exists in the spectra of the heat treated oxide films. Based on the above discussion we can reach the observation that the layer formed at the surface of GaAs by PEC method is really an oxide film of Ga and As. Therefore, the half reaction (1) could be rewritten as the following reaction:

$$2GaAs+6H_2O+12h^+ \rightarrow Ga_2O_3+As_2O_3+12H^+ \quad (2)$$

The glancing incident angle X-ray diffraction (GIXRD) measurement gives further information about the crystallography of the resulted GaAs oxide film. Figure 5 shows the diffraction patterns of the GaAs oxide films formed by PEC method. It can be seen that for the as-grown GaAs oxide film, no diffraction peaks can be found. It indicates that the as-grown oxide film has an amorphous structure. But the peaks of (401) Ga_2O_3, (111) β-Ga_2O_3 and (210) As_2O_3 occurred in the GIXRD spectra of the samples annealed at temperature 300℃ and 400℃. It indicates that the microstructure of the oxide films changed from an amorphous to a polycrystalline phase by the thermal treatment.

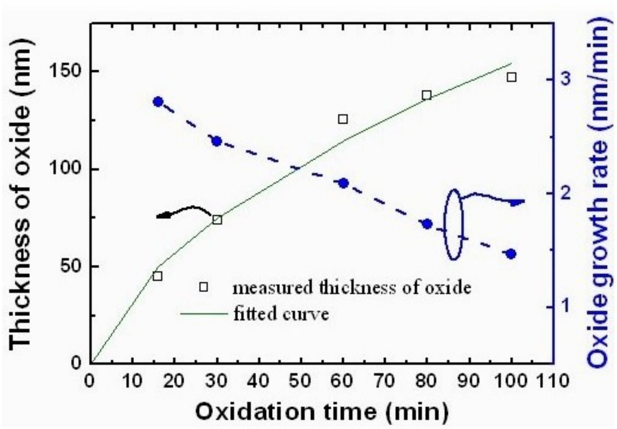

Fig. 2 The growth rate and thickness of the oxide layer produced on GaAs surface by PEC method at pH value of 3.5 as a function of oxidation time.

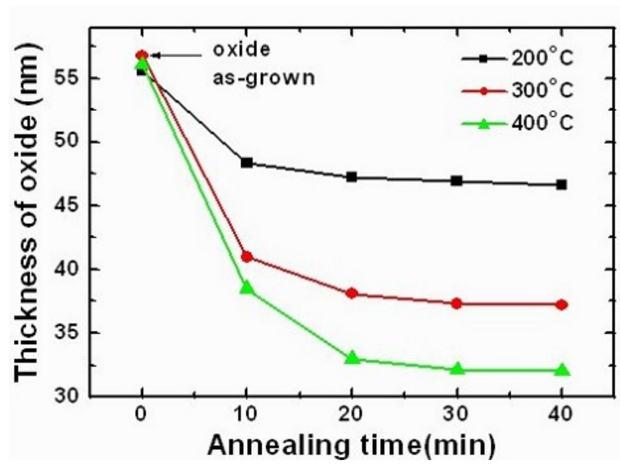

Fig. 3 Thicknesses of the oxide layers as a function of the thermal treatment time at various temperatures.

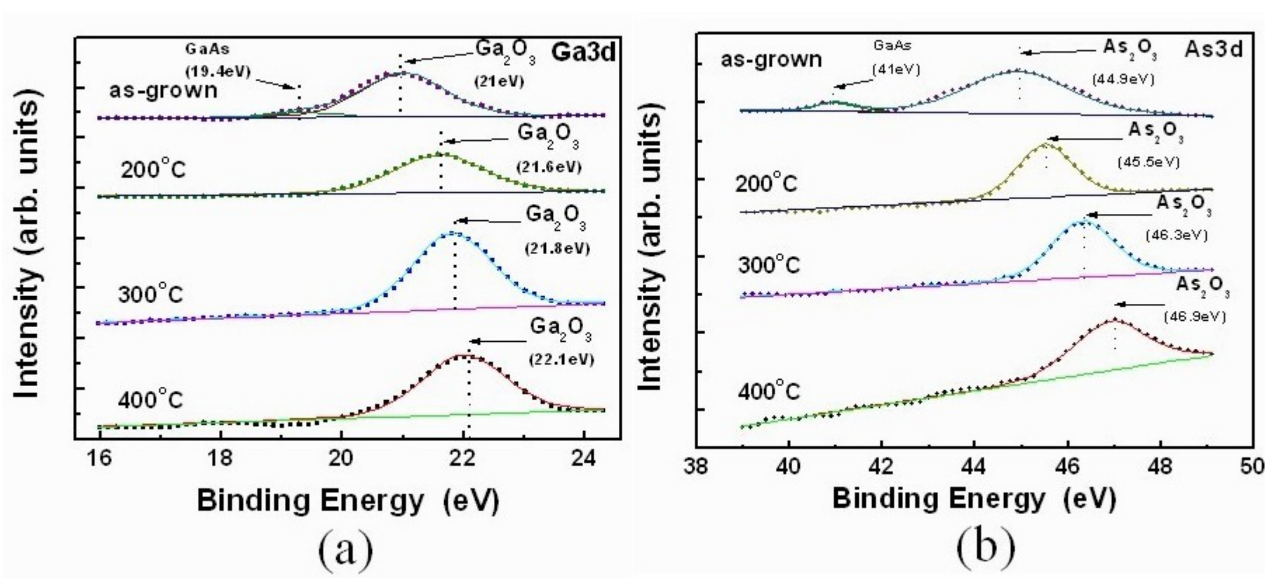

Fig. 4 XPS spectra for the core-level (a) Ga3d and (b) As3d of the PEC oxide layers, as-grown and annealed at various temperatures for 30 min.

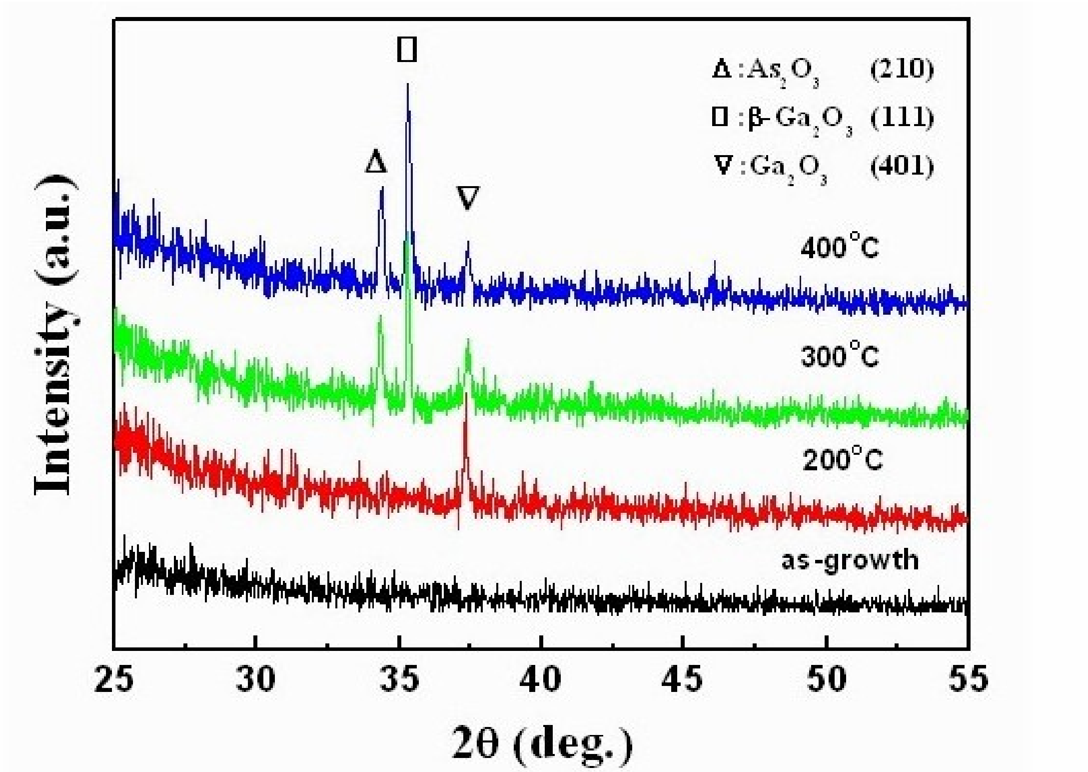

Fig. 5 X-ray diffraction patterns of the PEC oxide layers, as-grown and annealed at various temperatures for 30 min.

The photoelectrochemical oxidation method was successfully used to directly grow the GaAs oxide film on the GaAs surface. Only the pH value of about 3.5 is suited to directly grow the oxide layer on GaAs surface. From the experimental results of EDS, XPS and GIXRD, these results confirmed that the layer could be identified as Ga_2O_3 and As_2O_3, mainly the former. The PEC method is promising in oxide layer growth and all the fundamental information reported here about the method and the resulted oxide layers would be useful for developing new isolating layers in various semiconductor devices.

[1] E. H. Chen, D. T. Mclnturff, T. P. Chin, M. R. Melloch and J. M. Woodall, “Use of annealed low-temperature grown GaAs as a selective photoetch-stop layer”, *Appl. Phys. Lett.*, **vol. 68**, pp. 1678-1680 (1996).

[2] J. van de Ven and H. J. P. Nabben, “Anisotropic Photoetching of III-V Semiconductors”, *J. Electrochem. Soc.*, vol. **138**, pp. 144-152 (1991).