Study of diffusion barriers for Au metal on liquid phase oxidized GaAs

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TiW, TiN, Pd, and Mo as the diffusion barriers (DBs) in Au/DB/GaAs native oxide multilayer structures are investigated. The GaAs native oxides are prepared by liquid phase oxidation, and the results indicate that TiW and Mo films can effectively block Au diffusion at temperatures of up to 550 °C for 30 min. However, TiN and Pd films can effectively block Au diffusion only at 450 °C for 30 min. The failure of TiN and Pd appears related to the embedded oxygen in the barrier layers which cause the interdiffusion between Au and the barrier films. In comparison, TiW and Mo show better blocking properties that prevent Au from diffusing into oxide films. They also act as a diffusion barrier even at temperatures above 550 °C. © 2006 American Vacuum Society. [DOI: 10.1116/1.2366545]

I. INTRODUCTION

Native oxide layers grown on GaAs have attracted a lot of attention, resulting in many studies and investigations about them in recent years.1 Particularly, many complicated and expensive processes to grow native oxide layers on GaAs have been proposed. These include condensed gases,2 energy sources such as laser beams,3 optical illumination,4 electric potential,5 or magnetically excited plasma.6 However, the liquid phase chemical-enhanced oxidation (LPCEO) method performed at near room temperature is the latest processing technique which is simple and low cost and requires low temperatures.7–9 Moreover, gate oxide layers prepared by this method for GaAs, InGaP, and InGaAs-MOSPHETs have been successfully demonstrated10–12 to show superior device isolation performance.13 Specifically, the dielectric constant of LPCEO-grown oxide layers can be as low as that of an anodic oxide (~3.4),14,15 or even lower.16

In integrated circuit processing, as the device dimensions continue to shrink, the resistance-capacitance (RC) delay of interconnection becomes a serious problem.17 In order to reduce RC delay, low dielectric constant materials must be applied as interlayer dielectrics.18,19 In addition, oxide layers are usually employed as interlayer dielectrics for isolation in modern multilevel metallization structures. The interlayer dielectrics not only isolate the interconnection lines of different levels but also separate the active devices from the contact metals. As such, neither reaction nor interdiffusion between the contact metal and the dielectric layer is allowed during the thermal annealing of post-contact-metal-metallization or under the following processes. The diffusion of contact metal through the dielectric layer not only degrades the dielectric layer but also hinders device performance.20 Even for dielectric materials such as SiO2, a thin metal diffusion barrier is required to block contact metals such as Au, Al, Cu, and so on from diffusing into the dielectric materials.

In this article, a LPCEO-GaAs oxide layer was used as the dielectric layer. The thermal reactions between the contact metal and the LPCEO oxide layer were investigated using Au/GaAs oxide/GaAs metal-oxide-semiconductor structures with thermal annealing treatment. To prevent the contact metal from diffusing into the oxide layers under the thermal annealing of post-contact-metal-metallization, a diffusion barrier (DB) layer is formed between the Au metal and the LPCEO-grown oxide layer.

Several researches have reported the excellent performance of TiN films as a DB for GaAs Ohmic contact technologies.21,22 In addition, TiW and Mo films can also act as a good barrier layer for GaAs Ohmic contacts.23,24 Moreover, the Mo film is a better barrier layer than the TiN film in preventing copper diffusion into SiO2.25 The Pd film can keep its thermal stability as a DB between the titanium-based contact and the SiC after annealing at 600 °C for 30 min.26 Following the lead taken by the above research, TiN, TiW, Mo, and Pd are investigated in this study as diffusion barriers to prevent Au diffusion into oxide layers under thermal annealing.

II. EXPERIMENT

The substrates used in this study were 2 in. diameter n-type or semi-insulating epitaxial-ready (100) GaAs wafers. The oxidation system is simple and very low in cost which consists only of a temperature regulator and a pH meter. After performing standard cleaning, the GaAs wafers were immersed into the gallium-ion-contained nitric acid solution to form the oxidized layer. The high oxidation rate (1000 Å/h) is larger than that of the oxidation enhanced by boiling water (100 Å for 5 h). From the x-ray photoelectron spectroscopy analysis, the oxide layers were found to be composed of Ga2O3, As2O3, and AsO.16 The as-grown oxide layers have excellent chemical stability and stoichiometry, and their detailed oxidation processes have been presented in

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After oxidation, the samples were baked at 90 °C for 30 min. The barrier layers (TiN, Mo, TiW, and Pd) were then deposited on the LPCEO oxide layers in a radio frequency (rf) magnetron sputtering system at rates of 1.5, 10, 10, and 12 Å/s in an Ar-filled ambient, respectively. The thicknesses of the diffusion barriers (TiN, TiW, Mo, and Pd) and the Au metal are 70 and 100 nm, respectively. The TiN films were deposited by rf reactive sputtering from a Ti metal target, with the sputtering atmospheres filled with 80% Ar and 20% N2. The Au films were then deposited by a dc magnetron sputtering system using a water-cooled Au target with 99.99% purity in a pure Ar-filled ambient. Prior to the deposition, the targets were cleaned in a 5 min presputtering treatment. Under a base pressure of 3 \times 10^{-6} \text{Torr}, the deposition was carried out at room temperature without intentionally heating or biasing the substrate. The depositing dc power and pressure were 100 W and 4.3 \times 10^{-3} \text{Torr}, respectively. Thermal stressing was performed in a quartz furnace tube under N2-filled ambient. The annealing temperatures ranged from 300 to 550 °C.

In this work, scanning electron microscopy (SEM) was used to investigate the surface morphology of the samples, while Auger electron spectroscopy (AES) was used to analyze the in-depth distributions of the contact metal and the diffusion barrier metal for all the samples.

### III. POSTOXIDATION ANNEALING

In order to reduce the porous structure of the as-grown oxide layer and expel the trapped moisture, the samples were thermally treated at 250 °C for 30 min in a quartz furnace tube filled with high purity dry N2, the so-called “postoxidation annealing” in this work. The thermal stability of the Au/oxide/GaAs structure with and without postoxidation annealing was investigated by AES depth profiles, as shown in Fig. 1. The oxide film was about 860 Å thick with a refractive index of 1.65. Figures 1(a) and 1(b) show the AES depth profiles of the oxide film of the Au/oxide/GaAs structure without postoxidation annealing. Figures 1(c) and 1(d) show the AES depth profiles of the oxide film of the Au/oxide/GaAs structure with postoxidation annealing. For the oxide film without postoxidation annealing treatment, Fig. 1(b) reveals that the profiles of the 450 °C annealed Au/oxide/GaAs samples (for 1 min) at the Au-oxide interface were not as sharp as those of the as-deposited samples. This implies that diffusion occurred after annealing at 450 °C for 60 s. The Ga, As, and O profiles varied in similar distributions along the depth. However, the Au profile extension indicated that Au diffused into the oxide layer instead of Ga, As, and O diffusing into the Au metal. Meanwhile, the samples with postoxidation annealing and the 450 °C annealed Au/oxide/GaAs samples (for 30 min) after postoxidation annealing had very clearly separated interfaces. These sharp composition changes can be seen in Figs. 1(c) and 1(d), respectively. Au still slightly diffused into the oxide layer, however, indicating the requirement for a diffusion barrier to prevent the metal outdiffusion. In summary, comparing the AES depth profiles of the oxide films with and without postoxidation

![Fig. 1. AES depth profiles of the Au/oxide/GaAs structures at different annealing conditions: (a) as deposited, (b) annealed at 450 °C for 60 s, (c) postoxidation annealing of the oxide at 250 °C for 30 min, and (d) annealed at 450 °C for 30 min after postoxidation annealing of the oxide.](image-url)
annealing, it is found that postoxidation annealing can enhance the blocking property of the LPCEO oxide film against the diffusion of the Au metal.

IV. EFFECTS OF DIFFUSION BARRIERS

The surface morphologies of the Au/TiN/oxide and Au/Pd/oxide samples as deposited and after annealing at 450 °C are shown in Fig. 2. A very smooth surface can be seen in Fig. 2(a) for the as-deposited Au/TiN/oxide. Upon annealing at 450 °C, a good number of small voids were observed on the Au surface, as shown in Figs. 2(b) and 2(c). This was due to the diffusion of the upper gold layer into the diffusion barrier and the oxide layer.

Figures 3(a)–3(c) show the AES depth profiles of the Au/TiW/oxide samples as deposited and after annealing at 450 and 550 °C for 30 min. The AES depth profiles of the 450 and 550 °C annealed Au/TiW/oxide samples had the same distributions as the as-deposited ones. All of them had very clearly separated interfaces where sharp composition changes could be seen. These results demonstrate that the TiW layer can effectively block Au diffusion as the annealing temperature was increased up to 550 °C for 30 min. Moreover, the O profile of the 450 and 550 °C annealed samples had almost identical distributions as the as-deposited Au/TiW/oxide samples. Similar results can be seen in the Au/Mo/oxide samples of the AES in-depth profiles, as shown in Figs. 4(a)–4(c).
Figures 5(a)–5(c) show the AES depth profiles of the as-deposited and the 300 °C and 450 °C annealed Au/TiN/oxide structures. Due to the overlapping Ti (LMM$_3$) and N (KLL$_1$) Auger transition lines near 385 eV, the profiles labeled as TiN were deduced from the signals at 385 eV, and the profiles labeled as Ti were deduced from the signals at 420 eV. The AES depth profiles of Au and Ti on the as-deposited Au/TiN/oxide samples had the same Au and Ti profiles as the annealed samples at 300 °C. These results demonstrate that the TiN layer can block Au diffusion into the oxide layer. Significant interdiffusion between Au and TiN films is observed during the 300 °C, 30 min anneal. Figure 5(c) shows that after annealing at 450 °C for 30 min, however, oxygen and gold had significantly diffused into the TiN layer.

Figures 6(a)–6(c) show the AES depth profiles of the as-deposited and the 300 °C and 450 °C annealed Au/Pd/oxide structures. Upon annealing at 300 °C for 30 min, the distributions of the elements in the depth profiles indicated interdiffusion at the interfaces, as shown in Fig. 6(b). The interdiffusion of Au and Pd and the diffusion of Pd atoms toward the surface of the Au layer are obvious. The distribution of the Pd atoms at the Pd/GaAs oxide interface, however, was the same as that of the as-deposited samples. This result further demonstrates that the Pd does not diffuse into the GaAs oxide layer. By increasing the annealing temperature to 450 °C, the interdiffusion at the Au/Pd interface was further intensified. In addition, interdiffusion between Pd and GaAs oxide also became severe, as shown in Fig. 6(c).

V. CONCLUSION

The capabilities of TiW, Mo, TiN, and Pd films as diffusion barriers to block Au from diffusing in the Au/diffusion barrier/LPCEO oxide/GaAs system have been studied. The results indicate that TiW and Mo films can effectively block...
Au diffusion at temperatures of up to 550 °C. In comparison, TiN and Pd barrier layers fail at temperatures below 450 °C due to the oxygen incorporation into the barrier layers and Au interdiffusion. Mo and TiW are therefore superior materials for forming the diffusion barrier for Au and LPCEO oxide layers.

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