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Diffusion barrier layers for Al on GaAs native oxide grown by liquid phase chemical-enhanced oxidation

Jian-Jiun Huang [a], Dei-Wei Chou [b], Po-Wen Sze [c], Yeong-Her Wang [a,*]

[a] *Institute of Microelectronics, Department of Electrical Engineering, Advanced Optoelectronic Technology Center, National Cheng-Kung University, Tainan 701, Taiwan*
[b] *Department of Aviation and Communication Electronics, Air Force Institute of Technology, Kaohsiung 820, Taiwan*
[c] *Department of Electrical Engineering, Kao-Yuan University of Technology, Lu-Chu, Kaohsiung 821, Taiwan*

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Abstract

Thin films of TiW, TiN/Ti, Pd, and Mo as the diffusion barriers (DB) interposed between the Al layer and GaAs native oxide are examined. The GaAs native oxides are prepared by liquid phase oxidation. The interdiffusion of the Al/GaAs-oxide and Al/DB/GaAs-oxide (DB = TiW, TiN/Ti, Pd or Mo) multilayer structures are investigated by secondary ion mass spectroscopy, X-ray photoelectron spectroscopy, and Auger electron spectroscopy (AES). The results indicate that TiW and Mo films can effectively block Al diffusion and maintain their structural integrity up to 500 °C and 400 °C for 30 min, respectively. However, the thermal stability of TiN/Ti and Pd films cannot be maintained at 400 °C for 30 min. Moreover, the failure of TiN/Ti barriers due to oxygen incorporated into the barrier layers is observed and the failure of the Pd as the diffusion barrier in the interdiffusion between Al and GaAs oxide, as demonstrated by AES analyses, is also observed.

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1. Introduction

The application of oxide layers in GaAs-based circuit applications has attracted considerable attention [1]. Accordingly, many methods to grow the native oxide layers of GaAs, such as using condensed gases [2], laser beam [3], photo excitation [4], electric potential [5] or magnetically excited plasma [6], have been proposed. However, most of these methods have limited applications due to their expensive apparatuses or complicated processes. In this study, the GaAs oxide is prepared by means of an innovative, simple, low-cost, and non-energy-assisted processing technique which is called the liquid phase chemical-enhanced oxidation (LPCEO) method operated at near-room-temperatures [7–9]. According to previous results, the GaAs native oxide film prepared by LPCEO method is composed of Ga_2O_3, As_2O_3 and AsO [9]. It is also found that the dielectric constant of the LPCEO-grown oxide can be as low as that of the anodic oxide, ~3.4, [10–12] or even lower [13]. Moreover, the GaAs native oxides as dielectric gate applications for GaAs MOSFET [14,15] have also demonstrated good device performance and isolation. However, the gate metal diffusion into the oxide layer may degrade the device performance.

Oxide layers are likewise usually employed as the interlayer dielectric insulator in multilevel metallization

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[*] Corresponding author. Tel.: +886 6 2757575; fax: +886 6 2080598.
E-mail address: yhw@eembox.ncku.edu.tw (Y.-H. Wang).

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structures; the interlayer dielectric insulator should not only isolate the interconnect lines of different levels, but also separate the active devices from the contact metals. As such, no reaction (or interdiffusion) between the contact metal and the enclosed dielectric layer is allowed during high temperature processing. The contact metal which diffuses through the dielectric layer will not only degrade the dielectric layer but also the device performance [16]. Even for dielectric materials such as SiO_2, a thin, metal diffusion barrier is required to block the diffusion of the contact metals (such as Au, Al, Cu, etc.) into the dielectric materials. In this study, the thermal reactions of the multiplayer structures such as Al/oxide/GaAs structures have been investigated. The purpose of going through high-temperature annealing is to accelerate the thermal reactions. To prevent contact metals from diffusing into oxide layers under the post-thermal annealing of the contact metal metallization, barriers layers consisting of TiN, TiW, Pd, and Mo, which have been used in metal/SiO_2 structures [17–23], will be implemented as the diffusion barriers in the Al/barrier layer/oxide/GaAs structures.

2. Experimental

In this study, 2-in. n-type or semi-insulating GaAs (1 0 0) wafers were used as the substrates for the preparation of native GaAs oxide. The oxidation system which consists of a temperature regulator and a pH meter is simple and low-cost [7]. After standard cleaning, the GaAs wafers were immersed into the gallium-ion-contained nitric acid solution to form the oxidized layers. A high oxidation rate (1000 Å/h) is relatively larger than that of the oxidation enhanced by boiling water (100 Å for 5 h). The as-grown oxide layers have excellent chemical stability and stoichiometry. The detailed oxidation processes can be seen in [7,8]. After oxidization, the samples were baked at 90 °C for 30 min to densify the porous structure of the as-grown oxide layer and to cause the absorbed moisture to evaporate. Then post-oxidationannealing at 250 °C was conducted for 30 min in a quartz furnace tube filled with high-purity, dry N_2. Prior to deposition, a 5 min pre-sputtering was performed to clean the targets. Without specification, all the samples used here are 86 nm thick with a refractive index of 1.65 after post annealing.

The barrier layers consisting of TiN/Ti, Mo, TiW, and Pd were deposited on the LPCEO-oxide layer in a radio frequency (RF) magnetron sputtering system at the rates of 1.5, 10, 10, and 12 Å/s in a pure Ar atmosphere, respectively. Finally, Al metal was deposited also by RF sputtering. Under a base pressure of 3×10^{-6} Torr, the deposition was carried out at room temperature without heating or biasing the substrate. The depositing conditions are 100 W of DC power and 4.3×10^{-3} Torr of pressure. The thickness of the barrier metals (TiN/Ti, TiW, Mo, Pd) and Al is 70 and 100 nm, respectively. The TiN layers were deposited by RF reactive sputtering from a metal Ti target. The sputtering atmosphere for TiN was a mixture of 80% Ar and 20 N_2. The thermal annealing treatment was performed in a quartz furnace tube in ambient N_2. The annealing temperatures ranged from 300 °C to 550 °C. Before the samples were heated, the furnace tube was flushed with N_2.

The interdiffusion between the Al/oxide/GaAs or Al/DB/oxide/GaAs (DB = TiW, TiN/Ti, Pd, or Mo) was analyzed by a CAMECA IMS-5F SIMS system, with a double focusing mass spectrometer and X-ray photoelectron spectroscopy (XPS). The compositional depth profiles of the Al/DB/oxide/GaAs structures were performed by Auger electron spectroscopy (AES) using a Fisco Microlab 310D system. Ar was used as the ion source.

3. Results and discussion

It has been found that the post-oxidation annealing plays an important role in the oxide film properties [12]. In order to demonstrate the post-oxidation annealing effect on the masking capabilities of the GaAs oxide films against the diffusion of metal Al, the SIMS depth profiles of the Al/oxide/GaAs structure for the oxide film without the post-oxidation annealing are shown in Fig. 1 at different annealing conditions. As-grown oxides of 96 nm thick with a refractive index of 1.62 were used for the measurements, and the corresponding profiles are shown in Fig. 1. The XPS depth profiles of the Al/oxide/GaAs structure for the oxide films with the post-oxidation annealing are shown in Fig. 2a–c. For the oxide film without the post-oxidation annealing treatment, according to the depth profiles (not shown), no diffusion of Al was found for the annealing temperature of 120 °C for up to 65 min. Metal Al began to diffuse into the GaAs oxide after annealing at 150 °C for 1 min (Fig. 1). Moreover, the Al has already diffused through the GaAs oxide after annealing at 250 °C for 1 min. This implies that diffusion and/or reactions have begun to occur after annealing at 250 °C for 1 min. Obviously, the diffusion of Al into the oxide layer was significant at 500 °C, even for 1 min annealing time. Temperature seems to play a more important role in the metal diffusion. It indicates the requirements of the diffusion barriers for the following device processing. Based

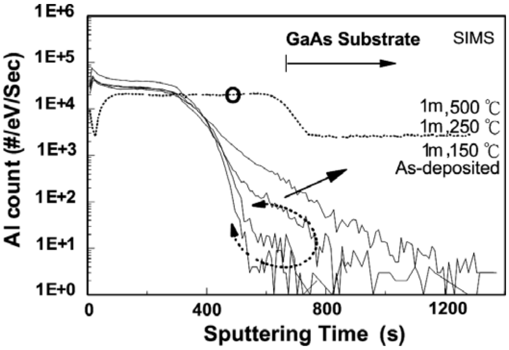

Fig. 1. The SIMS depth profiles of Al/oxide/GaAs structures without post-oxidation annealing treatment at various annealing temperatures and time.