Effect of Al Content, Substrate Temperature and Nitrogen Flow on the Reactive Magnetron Co-sputtered Nanostructure in TiAlN Thin Films Intended for Use as Barrier Material in DRAMs

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TiAlN thin films were deposited by using the reactive magnetron co-sputtering method with individual Ti and Al targets, where the Ti and the Al targets were simultaneously powered by using DC and RF sources, respectively. The electrical resistivity and the structural and microstructural properties of the deposited TiAlN thin films and the effects of Al content, substrate temperature and nitrogen gas flow rate on those properties were investigated. At a low flow rate of nitrogen gas (0.51 sccm), the electrical resistivity of the films was found to increase with increasing AC power, but at a high flow rate of nitrogen gas, it was found to decrease. The structural and microstructural analyses performed by using X-ray diffraction and scanning electron microscopy (SEM) showed that with increasing substrate temperature from room temperature to 400 °C, the films prepared at 400 °C have a crystalline structure while those prepared at room temperature had an amorphous nature. Also, the SEM analysis revealed that with decreasing AC power and increasing nitrogen flow rate, the size of the grains in the prepared films become larger.

I. INTRODUCTION

Titanium aluminium nitride (TiAlN) has been known as a coating material over the last decades [1]. This substance, due to its showing unique mechanical properties such as higher hardness, super wear resistance, lower thermal expansion, lower thermal conductivity and enhanced erosion resistance, has been widely used as protective hard coating [2,3]. If TiAIN coatings are exposed to air at higher temperatures, they form a TiO2 sub-layer and a dense, protective Al2O3 up-layer [4,5]. Therefore, the anti-oxidation temperature of TiAIN is higher than those of transition-metal nitrides such as TiN, NbN, ZrN [3,6].

TiAIN coatings have many applications. For example, TiAIN coatings can be used as node electrode barriers for complementary metal-oxide-semiconductor (CMOS) memory devices [7] or for temperature control in satellites [8, 9]. Recently, this material, due to its good thermal stability, diffusion barrier feature, and high oxidation resistance, has been suggested as a strong candidate for barriers in dynamic random access memory (DRAM) devices [10]. TiAIN, compared with other ternary barriers such as (Ti, Ta, W)-Si-N and W-B-N, shows a high oxidation barrier and a relatively low resistivity [6,10]. For TiAIN deposition, many different methods, such as cathodic arc plasma evaporation, plasma-assisted chemical-vapor deposition (PACVD) [11], ion-plating and DC or RF sputtering methods [12–14], have been used. Among these methods, magnetron sputtering has been attracting more attentions due to its higher deposition rate.

The purpose of this article is to discuss the optimal conditions for using as a barrier material in DRAM devices TiAIN films, deposited by using the reactive (DC, RF) magnetron co-sputtering method. In the sputtering method, the physical and the structural properties of deposited films depend highly on the substrate temperature, the substrate material, the energies and the types of sputtering particles, the bias, the gas pressure, the nitrogen flow and the sputtering power [15–17]. However, in this research, only the effects of the Al content, the substrate temperature and the nitrogen flow on the electrical properties of TiAIN thin films were studied.

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II. EXPERIMENTS

The titanium-aluminium-nitride films were deposited on quartz substrates by using a reactive magnetron co-sputtering system that has been described in detail elsewhere [18, 19]. Metallic titanium (99.99%) and aluminium (99.99%) targets with 3 in diameters were used for deposition. In this system, the Ti and the Al targets were simultaneously powered by using DC and RF sources, respectively. Before the substrates were placed sputtering chamber, they were cleaned in an ultrasonic system with acetone and ethanol, each for 15 min, and deionized water twice for 15 min. they were dried by using compressed air after each cleaning process. The distance between the targets and the substrate was about 20 cm. The base pressure of the sputtering system was lower than 5 × 10⁻³ Pa, which was obtained by using a turbo-molecular pump backed by a rotary pump. After Ar and N₂ had been introduced as sputtering and reactive gases, respectively, the pressure was kept at 2 × 10⁻¹ Pa for the sputtering. The flow of both gases was controlled by using MKS mass flow controllers to keep the total sputtering pressure constant. After the chamber pressure had been adjusted, Al and Ti targets were sputtered by using Ar ions in a mixed Ar – N₂ atmosphere, with two different values of P (N₂) during the sputtering process. During the deposition process, the sum of the DC and the RF powers was constant at 500 W. All films were deposited at substrate temperatures of 400 °C and room temperature. The deposition rate was varied by varying the DC and the RF powers and the nitrogen flow. The thicknesses of films were kept about 100 nm by adjusting the deposition time. For deposition, a mask with dimensions of 3 × 12 mm² was used; therefore, the deposited films had the same surface areas.

For electrical resistivity measurements, a four-point probe device was used. The phases and the structural properties of the deposited films were determined by using X-ray diffraction (XRD: D500, Siemens, German) and microstructure analyses with Scanning electron microscopy (SEM: FEG MIRA3, Tescan, Czech), respectively.

III. RESULTS AND DISCUSSION

Four sets of films were prepared under different deposition conditions. In the first set, films were deposited on substrates at room temperature with a 0.51-sccm nitrogen flow, the second set was deposited on substrates at room temperature with a 2.78-sccm nitrogen flow, the third set was deposited on substrates at 400 °C with a 0.51-sccm nitrogen flow, and the fourth set was deposited on substrates at 400 °C with a 2.78-sccm nitrogen flow. The results are given in Tables 1 to 4. In all sets, the argon flow was 18 sccm, and the film’s thickness was about 100 nm.

### Table 1. Electrical resistivities of the first set of films deposited on substrates at room temperature with a 0.51-sccm nitrogen flow for different DC and RF powers

| Sample | DC power (W) | AC power (W) | Electrical resistivity (kΩ) |
|--------|--------------|--------------|---------------------------|
| A₁₁    | 120          | 380          | 0.044                     |
| A₁₂    | 200          | 300          | 0.125                     |
| A₁₃    | 300          | 200          | 4.530                     |
| A₁₄    | 380          | 120          | 1.060                     |

### Table 2. Electrical resistivities of the second set of films deposited on substrates at room temperature and with a 2.78-sccm nitrogen flow for different DC and RF powers

| Sample | DC power (W) | AC power (W) | Electrical resistivity (kΩ) |
|--------|--------------|--------------|---------------------------|
| A₂₁    | 120          | 380          | > 50                      |
| A₂₂    | 200          | 300          | > 50                      |
| A₂₃    | 300          | 200          | > 50                      |
| A₂₄    | 380          | 120          | > 50                      |

#### 1. Electrical Resistivity

In Tables 1-4, results concerning the resistivity measurements for the four sets of deposited films are presented. As represented in Table 1, the electrical resistivity decreased with increasing RF power because with increasing RF power, the number of sputtered Al atoms within the chamber increased, but the nitrogen flow was low; therefore, some of the Al atoms could interact with the nitrogen molecules. Thus, most of the sputtered Al atoms individually participated in the film composition. Because each aluminium atom can contribute three valence electrons, with increasing AC power, the number of Al atoms and, consequently, the number of carriers in the prepared film increase, leading to a decreased resistivity.

The electrical resistivity of the second set of deposited films prepared with a 2.78-sccm nitrogen flow was so large that our four-point probe device was unable to measure the electrical resistivities of these films. As mentioned above, when the increasing nitrogen flow was increased, the interactions between Al and N₂ atoms also increased; on the other hand, according to the XRD patterns (Fig. 1), this set of films had an amorphous nature; therefore, the mean free path of the carriers was reduced and the carriers could not move easily through the films. For these reasons, the electrical resistivities of the films were very high.

According to Table 3, the electrical resistivities of the films decreased with increasing AC power. As the AC power was increased, the number of sputtered Al
atoms also increased; thus, due to the low flow of $N_2$ gas injected into the chamber, reactions between nitrogen molecules and Al atoms decreased so the prepared films were a mixture of metallic nitrides ($AlN$, $TiN$) and metallic atoms (Al, Ti) in which the contributions of Al atoms were more. Thus, these films show quasi-metallic properties.

As shown in Table 4, the electrical resistivities decreased with increasing DC power; in other words, the electrical resistivity increased with increasing AC power. The reason for this is that $TiN$ is a good conducting material [20]; thus, with increasing DC power and high flow of nitrogen gas, the contribution of $TiN$ in the films will increase and the resistivity will decrease. Inversely, $AlN$ is a substance with a wide band gap [21]; thus, with increasing AC power and a higher flow (2.78 sccm) of nitrogen gas, the proportion of $AlN$ in the prepared films will increase, leading to higher resistivities. Comparing the results shown in Tables 1 and 3 for films prepared under the same deposition conditions, except for the substrate temperature which is different, we notice that with increasing substrate temperature from room temperature to 400 °C, the electrical resistivity is decreased. When the substrate temperature is low, atoms reaching the substrate do not have the necessary surface mobility for accommodation into special lattice positions, and upon reaching the substrate, they become frozen in their places [23]; in principle, any alloy, even a pure metal, can become amorphous if a sufficiently high cooling is used to cool it from the liquid state [24]. However, at higher temperatures due to the atoms having more surface mobility, they can move on the substrate’s surface to become accommodated in special lattice positions.

As the XRD patterns show, films prepared on substrates at room temperature do not have a crystalline structure and are in an amorphous phase while films prepared on substrates kept at 400 °C have solid solution phases and a crystalline structure.

### 2. X-ray Diffraction Analysis and Structure of the Coatings

Transition-metal nitrides can exist in various stoichiometric phases [25], and, $TiAlN$ may exist in the $Ti_2AlN$ and the $AlN$ phases. The formation of each phase

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**Table 3. Electrical resistivities of the third set of films deposited on substrate at 400 °C with a 0.51-sccm nitrogen flow for different DC and RF powers**

| Sample Code | DC Power (W) | AC Power (W) | Electrical Resistivity (kΩ) |
|-------------|--------------|--------------|-----------------------------|
| B11         | 120          | 380          | 0.0059                      |
| B12         | 200          | 300          | 0.0137                      |
| B13         | 300          | 200          | 0.0129                      |
| B14         | 380          | 120          | 0.0838                      |

**Table 4. Electrical resistivities of the fourth set of films deposited on substrate at 400 °C with a 2.78-sccm nitrogen flow for different DC and RF powers**

| Sample Code | DC Power (W) | AC Power (W) | Electrical Resistivity (kΩ) |
|-------------|--------------|--------------|-----------------------------|
| B21         | 120          | 380          | > 50                        |
| B22         | 200          | 300          | 3.889                       |
| B23         | 300          | 200          | 0.594                       |
| B24         | 380          | 120          | 0.309                       |

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strongly depends on deposition parameters such as the nitrogen partial pressure, the substrate bias, the substrate temperature, etc. [19]. The deposition conditions are shown in Tables 1 to 4. Because the deposition conditions consist of DC and RF powers and the substrate temperatures were same for sets 1 and 2 and for sets 3 and 4, the compositions and the microstructure of sets 1 and 2 will be similar to these of sets 3 and 4, only set 1 and set 4 were studied structurally.

Figure 1 shows the XRD patterns for the films of set 1, which were deposited under the conditions summarized in Table 1. As shown in Fig. 1, the films have an amorphous structure and did not exhibit peaks of the compounds. As mentioned above, the cause of the amorphous nature of these films was the high cooling rate. Due to that, the mean free path of carriers in these films is short, and carriers can not move between atoms easily; therefore, the electrical resistivities of these prepared films will be high.

Figure 2 shows the XRD patterns for the TiAlN films of set 4, where deposition conditions are summarized in Table 4. With increasing substrate temperature to 400 °C, some peaks appear, indicating that these prepared films have a crystalline structure. The preferred orientation of the grains has been found to depend on the mobility of the Ti, Al and N atoms. The mobility is a function of the energy of these atoms; with increasing substrate temperature to 400 °C, mobility becoming greater [26] and atoms can move on the substrate to a suitable lattice sites. This will cause a significant change in the surface morphologies of the films and the films will grow in some planes that have higher atomic density.

3. Microstructure of the Coated Films

The microstructures and the surface morphologies of the (Ti, Al) N coatings deposited at different deposition conditions are illustrated the by SEM micrographs shown in Fig. 3. As shown in Fig. 3, samples A_{22} and B_{22}, which were prepared with a nitrogen flow (2.78 sccm), possess compact, and denser surfaces compared with samples A_{12} and B_{12}, which were prepared with a low nitrogen flow (0.51 sccm). With increasing N_{2}/Ar ratio, the grains become denser, and the surfaces appear smoother. This indicates that the deposition rate is decreased significantly with increasing nitrogen partial pressure. This results from the decreasing sputtering yields of Al and Ti because the Ar-ion density decreases at higher N_{2}/Ar ratio [2]. Also, the TiAlN coatings clearly show different structures, due to the presence of the AlN phase at a high N_{2}/Ar ratio. The hexagonal AlN phase interrupts the cubic TiAIN [2].

The grain size in the deposited films was about 10 – 30 nm, as obtained from the SEM micrographs. This result is in good agreement with the values obtained from the Scherrer relation \( L_{hkl} = \frac{0.94 \lambda}{\beta \cos \theta} \). With regards to the Scherrer relation in which the full width at half maximum is used, one can only calculate the grain size in films having crystalline structure. The values obtained from this relation for the films with crystalline structures were in the range of 20 – 30 nm.
IV. CONCLUSION

The effects of the Al content, substrate temperature and nitrogen gas flow rate on the electrical resistivity, structure and microstructure of TiAlN films prepared by using a magnetron co-sputtering system have been investigated. The basic conclusions are as follows:

1. For low flows of nitrogen gas, the electrical resistivity of the prepared films decreased with increasing AC power. With increasing AC power, the number of sputtered Al atoms within the chamber increased, but due to the low nitrogen flow, no Al atoms interacted with the nitrogen molecules; thus, most of the Al atoms individually participated in the film’s composition. Each aluminium atom contribute three valence electrons; therefore, with increasing AC power, the number of Al atoms, and consequently, the number of carriers in the prepared film increased, leading to a resistivity decrease. However, for high flows, the electrical resistivity increased with increasing AC power. With increasing AC power and a higher flow of nitrogen gas, the proportion of AlN in the prepared films increased, leading to higher resistivities because AlN is a wide band gap substance.

2. When the substrate temperature was increased from room temperature to 400 °C, as the XRD patterns show, the films prepared on substrates kept at 400 °C had a crystalline structure and the electrical resistivities in these films were lower than they were in films prepared on substrates kept at room temperature. Due to having more surface mobility at higher temperatures, they can move on the substrate’s surface to become accommodated in special lattice positions; therefore, carriers can move easily between the atoms of the prepared films.
3. The surfaces of the films prepared in a higher nitrogen flow were denser than the surfaces of the films prepared in low flow of nitrogen gas, which is thought to be due to the significant decrease in the deposition rate with increasing nitrogen partial pressure.

4. The grain sizes in the constituent films, according to SEM micrographs, were about 10 – 30 nm, and the larger grain size was related to a higher nitrogen flow.

5. TiAlN coatings prepared under the deposition conditions of a DC power of 120 W, an AC power of 380 W, a nitrogen flow of 0.51 sccm, and a substrate temperature of 400 °C had the lowest electrical resistivities and was the best coating for use as a barrier material in DRAM devices.

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