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Preparation of ultrathin TiN_x films by radical assisted low temperature deposition and their barrier properties against Cu diffusion

Mayumi B. Takeyama [a, *], Masaru Sato [a], Eiji Aoyagi [b], Atsushi Noya [a]

[a] Department of Electrical and Electronic Engineering, Faculty of Engineering, Kitami Institute of Technology, Kitami 090-8507, Japan
[b] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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ABSTRACT

We examine characterization and barrier properties of the TiN_x films prepared by an original deposition method, which consists of conventional sputtering and radical treatment. This method realizes the low-temperature deposition of the diffusion barriers applicable to Cu-through silicon via (TSV) in the three-dimensional large scale integration (3D-LSI) of wafer on wafer process. We can successfully prepare the TiN_x films of low resistivity and high density at a temperature lower than 200 °C. The 5-nm-thick TiN_x films as the diffusion barrier for Cu-TSV show sufficient performance to the thermal stress without interface layers owing to solid-phase reaction and intermixing after annealing at 500 °C for 30 min at both Cu/TiN_x and TiN_x/SiO_2 interfaces. The proposed method in this study is a candidate process for depositing the transition metal nitride film at low temperatures in the 3D-LSI.

1. Introduction

Strong requirements for obtaining thin films at low deposition temperatures have come about in many applications of three-dimensional large scale integration (3D-LSI) [1,2], solar cells [3,4], liquid-crystal displays [5], and so on [6–8], in order to decrease thermal damages in precision thin-film assemblies. However, a decrease of the deposition temperatures sometimes results in a deterioration of film quality. Therefore, it is generally difficult to obtain thin films of high-performance at low temperatures.

In the case of an application of through silicon via (TSV) interconnects in the 3D-LSI technology so-called wafer on wafer process, both an insulating barrier (such as a SiN_x film) and a diffusion barrier (such as a TiN film against penetration of copper (Cu) buried within a via), which cover up the side wall of the via, as schematically shown in Fig. 1, must be deposited at low temperatures below 200 °C [1,2]. This is because the TSV process must be executed at a temperature not to deteriorate completed LSI. This is also because a wafer is stacked on another wafer using an organic adhesive material at maximum permissible temperature below 250 °C in the wafer bonding process for via-last integration [9].

In a previous study, we have demonstrated the preparation of high performance SiN_x films without substrate heating [10–12]. In addition to this, if we can succeed in the deposition of a diffusion barrier at low temperatures, a thin film couple of an insulating barrier and a diffusion barrier applicable to TSV can be realized. We have reported the preliminary examination of the low-temperature deposition of a zirconium nitride (ZrN_x) film as a diffusion barrier [13]. Usually, the thermal energy as the substrate temperature is necessary to form the transition metal nitride film by reactive sputtering. However, we obtained the ZrN_x films without substrate heating by using the activated radical species.

In this article, we chose titanium nitride (TiN_x) films as a candidate barrier material in order to examine the characterization of the TiN_x films obtained by the proposed method. Thin TiN_x films have been conventionally used as a typical diffusion barrier so far, and therefore, there is a considerable amount of literature to compare the characterization as a barrier between the present study and others [14–19]. In addition, the existence of oxygen in the ZrN_x films was confirmed in the previous study [13]. We expect that the oxygen incorporation in the films could be controlled by changing the prepared material from ZrN_x to TiN_x, by comparing the values of diffusion coefficient and activation energy of nitrogen and oxygen atoms in the films of ZrN_x and TiN_x [20].

We can suppress the process temperature lower than 200 °C by

* Corresponding author. Tel.: +81 157 26 9288; fax: +81 157 26 9260.
E-mail address: takeyama@mail.kitami-it.ac.jp (M.B. Takeyama).

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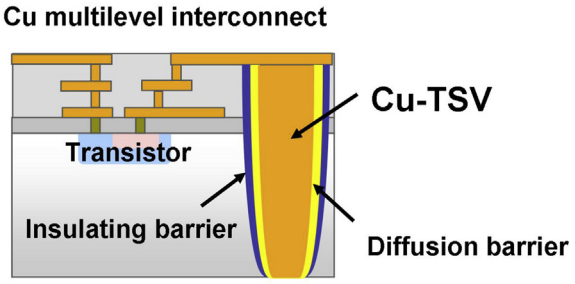

Fig. 1. Schematic cross-section of the Cu-TSV.

optimizing the above-described procedure. We also examine the barrier properties of the obtained TiN_x films in the $Cu/TiN_x/SiO_2/Si$ TSV model structure. We can successfully demonstrate the good barrier properties of the TiN_x films deposited at low temperatures.

2. Experimental details

An apparatus using the present experiments is schematically shown in Fig. 2, where in a vacuum chamber evacuated by an oil-diffusion pump, a deposition-up type conventional RF (13.56 MHz) sputtering system with a 2 inch in diameter cathode was placed. A tungsten wire, 99.9% purity, 0.5 mm in diameter and 0.3 m in length, was placed surrounding the cathode. Fig. 3 shows the schematic process flow of a proposed deposition method. The chamber was evacuated to a base pressure of ~2.7×10^{-5} Pa.

1. First, a thin Ti film (2–3 nm in thickness) was sputter-deposited on a thermally grown SiO_2 (100 nm)/Si substrate at room temperature with an Ar sputtering gas pressure of 5.3 Pa. A Ti (99.99% purity) target was used for sputtering with an RF power of 50 W.
2. Then, the gas atmosphere was changed from Ar to NH_3 (99.9% up purity) at a pressure of 1 Pa, and the W-wire was electrically heated (applied voltage of 6.5–9.5 V) to a certain temperature (1400–1700 °C) to catalytically decompose NH_3 molecules to radical species, which react with a thin Ti film to form TiN_x. We denote these processes as 'one cycle'. The temperature of the W-wire was measured by two color irradiation thermometer of impac company. Radical treatment was performed during 1–5 min by one cycle, and the substrate temperature increase owing to irradiation from the heated W-wire was 100–450 °C
3. Then, the above-described cycle was repeated to obtain the film with a desired thickness (5–20 nm in thickness).

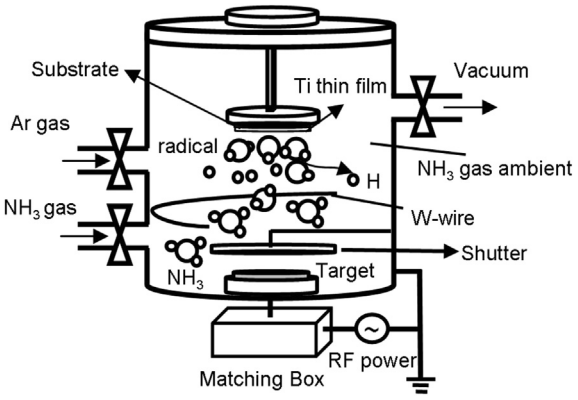

Fig. 2. Schematic illustration of the present deposition system placed a tungsten wire.

The TiN_x film was taken out from the chamber and a Cu overlayer was deposited in a DC tetrode sputtering system at room temperature to complete Cu (20–100 nm)/TiN_x(5–20 nm)/SiO_2(100 nm)/Si specimens. The Cu target (99.999% purity, 50 mm × 50 mm × 1 mm^t) was used, and the sputtering voltage and current during the Cu deposition were 500 V and 70 mA, respectively. Some specimens were subsequently annealed at various temperatures up to 500 °C in a vacuum of 10^{-5} Pa for 30 min.

Electrical characteristics were measured by a four-point probe method by using a 20 nm-thick TiN_x film. X-ray diffraction (XRD) and grazing incidence X-ray reflectivity (GIXR) measurements were conducted by using a PANalytical X'Pert MRD with a collimated parallel beam by an X-ray mirror with a Cu Kα radiation source, operating at 45 kV and 40 mA. A high voltage transmission electron microscopy (TEM) (JEM-ARM 1250) operating at an acceleration voltage of 1250 kV was used to characterize the structure and texture in the obtained TiN_x films and $Cu/TiN_x/SiO_2/Si$ specimens. Chemical bonding states of the layers were analyzed by using a JEOL JPS-9200 X-ray photoelectron spectroscopy (XPS) equipped with an Al monochromatic X-ray source. Here, we mention the sample preparation for the XPS analysis. The Cu layer (20 nm) was deposited on the TiN_x films to form the Cu(20 nm)/TiN_x(5–17 nm)/SiO_2/Si configuration to avoid the oxidation and to obtain certain ground potential of the sample surface to the apparatus. Then, the Cu surface was etched by Ar-ion to obtain Ti and N signals through the remaining Cu layer. We use the obtained binding energy of Cu 3d spectrum as a reference to determine the chemical shift of each element.

3. Results and discussions

3.1. Characterization of the TiN_x films

First, we examined the conditions of the W-wire temperature for the suitable radical reaction to obtain TiN_x films. Umemoto et al. [21] reported that decomposition products by the catalytic cracking of NH_3 molecules on the heated W surface are NH_2^* radicals and H atoms; this process occurs at about 1000 K of a W-wire temperature and the number of products increases with increasing the W-wire temperature to about 2000 K, and the number of products is then saturated at higher temperatures. According to this experiment, the main radical species obtained in our experiments are also considered to be NH_2^* radicals.

Fig. 4 shows grazing incidence XRD patterns (thin film mode) of the obtained TiN_x films of 20 nm in thickness for various radical treatment times. Here, the W-wire temperature is set at 1700 °C. From the specimen before the radical treatment, the reflection lines corresponding to Ti are observed. On the other hand, from the obtained film after radical treatment, the reflection lines from TiN(111) and (200) planes are observed regardless of the radical treatment time. It is demonstrated that the TiN_x films are obtained by the radical treatment at the Ti surface. However, intensity of reflection lines from TiN becomes weak with increasing the radical treatment time. In the specimen radical treated for 5 min, the substrate temperature increased to 450 °C. An increase in the substrate temperatures generally brings about a certain formation of the Ti–N chemical bonding and good characterization by reactive sputtering method, but the present method shows contradictory temperature dependence. To clarify this reason, we examined the chemical states of elements in the obtained TiN_x films by XPS analysis.

We show typical results of the XPS spectra obtained from the TiN_x films prepared by different W-wire temperatures of about 1700 °C (high wire temperature) and 1400 °C (low wire