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The effect of thermal treatment on the electrical properties of titanium nitride thin films by filtered arc plasma method

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Abstract

In this work, the titanium nitride (TiN) films were prepared by filtered arc plasma (FAP) method with thickness ranging from 7 to 75 nm. The structure of TiN film was determined by X-ray diffraction (XRD). Sheet resistance ($R_\square$) and TCR were measured by four-point probe station and TCR measurement system respectively. The results indicate that $R_\square$ and TCR of TiN films are strongly thickness-dependent. After annealed above their individual critical temperature (T_c), all films experienced huge resistance increases and color variations. While annealed below T_c, most of TiN films exhibited better resistance stability and repeatability than as-deposited TiN film. For extremely thin TiN film, like 7 nm, after annealed below T_c, its TCR turned from positive to negative. T_c for different TiN film was found strongly thickness-dependent from 200 to 600 °C.

Keywords: C. Electrical properties; Filtered arc plasma; TiN thin film; Annealing

1. Introduction

Titanium nitride (TiN) thin films have been widely used in semiconductor industry based on their good material properties, such as extreme hardness, high melting temperature, and golden color as decorative coating [1–3]. In recent years, TiN film has been found a new application. Due to its relatively low temperature coefficient of resistance (TCR) and excellent resistance stability especially at high temperature, TiN film is being considered as a promising material for micro-heater in infrared (IR) emitter applications [4,5].

Many studies revealed that material properties of TiN films are strongly dependent on the deposition method and process conditions. In this work, TiN was deposited by filtered arc deposition (FAD) technique, which permits the production of TiN film free of micro-droplets and with smooth film surface. The description of FAD system and its process can be seen in many papers published over the last decade [6].

This paper studies the electrical properties of TiN films before annealing process and after annealing process. The effects of annealing temperature on different TiN films are investigated with the aids of TCR measurement results, X-ray diffraction (XRD) patterns and visual inspection.

2. Experimental procedures

2.1. Preparation of TiN films

Silicon (1 0 0) coated with a layer of 500 nm SiO_2 and a subsequent 200 nm insulating Si_3N_4 layer is used as the substrate. TiN film was deposited on the substrate by filter arc plasma (FAP) method. Prior to the deposition, Ar ion beam with energy of 4000 eV was used to clean the substrate for about 15 min. A temperature rise of the substrate cause by ion bombardment was observed, and the maximum substrate temperature was recorded as 140 °C. The vacuum chamber was first pumped to a base pressure, and then a N_2 flow was fed into the chamber to reach the setting value of working pressure of 6.5×10^{-2} Pa. The arc current was fixed at 75 A and a constant bias voltage of −100 V was applied to the substrate. Samples S1–S4 were prepared with different deposition time as 20 s, 1, 2, and 3 min, respectively.

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2.2. Characterization

Sheet resistances ($R_\square$) of four samples were measured by four-point probe station and TCR were measured in a N_2 atmosphere by a computer-controlled hot stage together with a Keithley 236 source measurement unit. The hot-stage is hosted in a chamber for precise temperature and atmosphere control. TiN film thickness was estimated by Filmetric F-20 measurement system and the crystal structure was examined by X-ray diffraction technique with Cu Kα radiation. TiN films were annealed in N_2 atmosphere in a Lindburg quartz furnace. The maximum annealing temperature was 700 °C at the heating and cooling rate of 5 °C/min.

3. Results and discussion

In Fig. 1, the thickness of TiN film is proportional to the deposition time and $R_\square$ is inversely proportional to the thickness, as the deposition time exceeds 60 s. This relationship can be used to control the $R_\square$ of TiN film by precisely controlling the deposition time. Resistance variations of S1–S4 against temperature are plotted in Fig. 2. It shows the TCR of TiN film is strongly dependent on the film thickness and increases with the increased thickness. For S2–S4, in the temperature range of 300–550 K, the resistances increase with the temperature similar to that in metallic thin film. However, for S1 the resistance variation shows more complicated phenomenon. Below 450 K, positive and negative TCR were observed in different pieces from S1 group. Above 450 K, the resistance increases rapidly till infinity.

S1 also exhibited poor repeatability of TCR during multi-round tests. As shown in Fig. 3(a), S1 experienced positive TCR of 320 ppm/K in the first-round test and then turned to negative TCR of 64 ppm/K in the second-round test. These two TCR values approximate to the results of +326 ppm/K and −69 ppm/K in Fig. 2(b). Moreover, S1 showed large change in the starting resistance at room temperature for near 200 Ω in the first-round test and 575 Ω in the second-round test, respectively. By contrast, for S2–S4, the good TCR repeatability can be found in Fig. 3(b). After the first-round test, except for a slight resistance increase at

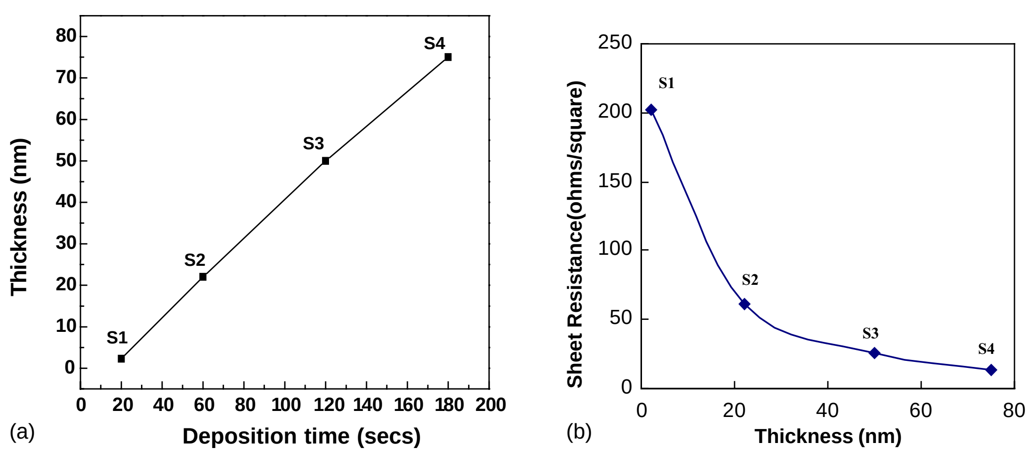

Fig. 1. The curves of (a) film thickness vs. deposition time and (b) sheet resistance ($R_\square$) vs. film thickness for S1–S4.

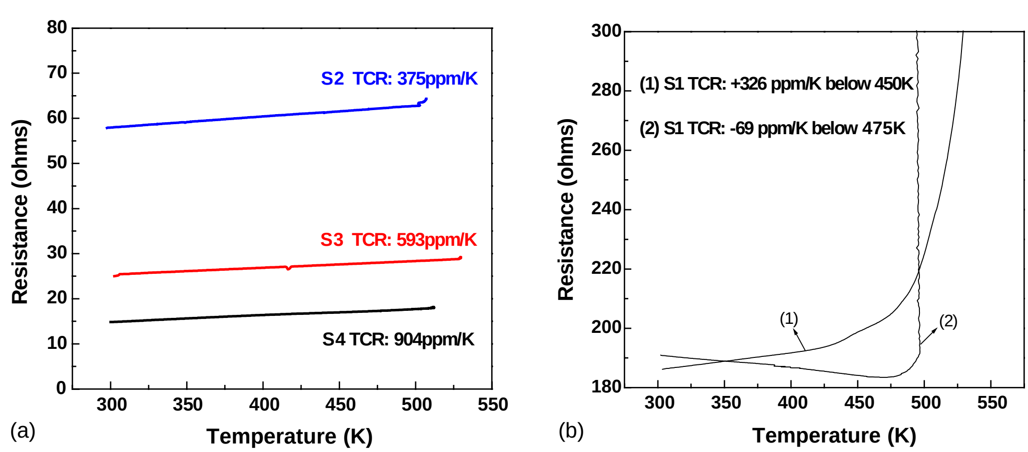

Fig. 2. Resistance vs. temperature for (a) S2–S4 and (b) S1.

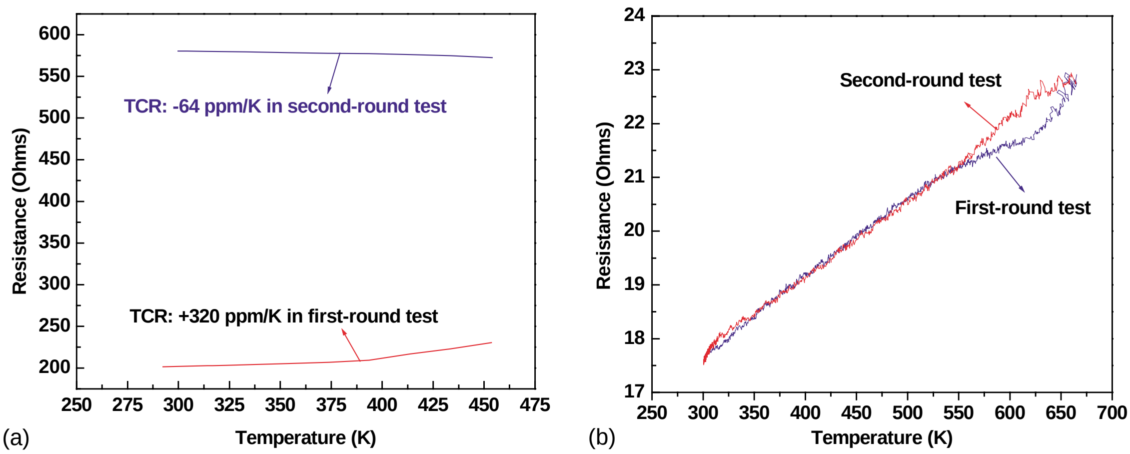

Fig. 3. The resistance variations of (a) S1 and (b) S4 against temperature during the first-round and second-round measurement, respectively.

high temperatures, no significant change in TCRs of S2–S4 was observed in the second-round test and there was a linear relationship between resistance and temperature. After the second-round test, TCR behavior remained unchanged. The possible reason for different TCR behaviors in S1–S4 will be explained by the theory of thin film formation.

Thin film formation involves the process of nucleation and growth [7], which can be divided into three distinct stages [8]. When a metal film is concerned, the electrical conduction mechanism in each stage is different. In the first 3-D island growth stage, due to the isolated island structure, the film shows the electrical properties of discontinuous metal films with electrical conduction associated with negative TCR. In the second growth stage, coalescence of islands occurs and electrical property of this film is expected to be an intermediate between the first and third stage. The third stage results in the formation of a true continuous film and electrical conduction for a continuous film is governed by the mechanisms of bulk conduction and surface scattering associated with positive TCR.

From the TCR behavior of S1 in Fig. 2(b), the TiN film is supposed in the second stage of growth; therefore, it displays both positive and negative TCR. Due to its metastable state, S1 also exhibited poor repeatability of TCR, as shown in Fig. 3(a). In Fig. 3(b), the small resistance increase at high temperatures in S4 after first-round test is due to the existence of defects in the film deposited at low temperature. The heat obtained from the first-round test helps to drive them out and improves the film thermal stability. As for the huge resistance increase at high temperatures in S1 in Fig. 2(b), it is attributed to either the film breakdown [9] or oxidation reaction [10].

In our experiments, the annealing temperature influenced the properties of TiN films gradually and the films from S1–S4 have similar behaviors against annealing temperature. As illustrated in Fig. 4 for S4, an obvious resistance increase was observed after the TiN film was annealed above 500 °C. The temperature with this turnover point is denoted as critical temperature (T_c). Besides S4, S1–S3 also experienced the obvious resistance increase after annealed above their individual T_c. T_c is apparently related to the film thickness, and the larger the thickness, the higher the T_c. As stated earlier, thin film deposited at lower temperature consists of many stable and small islands. Raising the temperature, the islands grow in size due to the agglomeration. Consequently, a continuous film deposited at low temperature becomes non-continuous after annealing [8]. This agglomeration will incur a large resistance increase in the film over a certain high temperature. Belser and Hicklin have reported there was a direct connection between the film thickness and the highest annealing temperature (T_c) before agglomeration [8]. However, the subsequent sharp resistance increase in the annealed-TiN film above T_c can only be explained by the oxidation reaction, which always occurs above 500 °C or so [10]. From experimental result, titanium oxide was found in the 500 °C annealed-TiN film, as shown in Fig. 5. In addition, besides the resistance variation, annealed-TiN film shows different color with the annealing temperature as shown in Fig. 6. The color change trend is from the original light yellow to golden yellow, bronze, and light blue, lastly purple color. The color change was caused

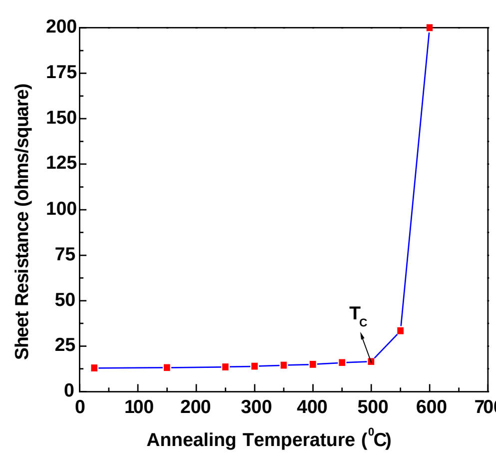

Fig. 4. Effect of annealing temperature on resistance of TiN film (S4).

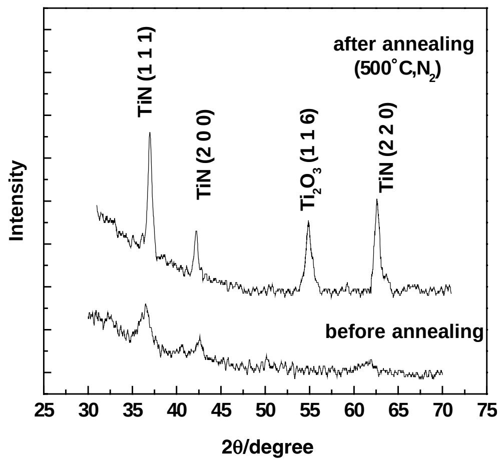

Fig. 5. XRD patterns of as-deposited TiN film and post-annealed-TiN film at annealing temperature of 500 °C in N_2 (S2).

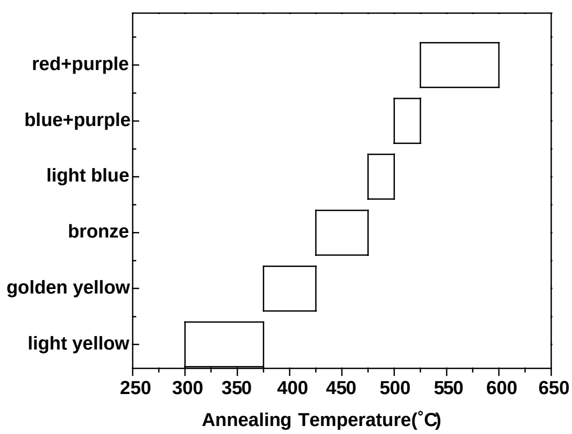

Fig. 6. The schematic of annealed-TiN film color change trend against annealing temperature (*X* axis: the correspond TiN film color).

either by the thickness change or the oxidation reaction in which different titanium oxide (TiO, Ti_2O, Ti_2O_3, etc.) can be formed at different annealing temperature stage.

4. Conclusions

Electrical properties ($R_\square$ and TCR) of TiN films are strongly thickness-dependent and they are stable for those films with thickness above 7 nm. As the film thickness less than 7 nm, the film is electrically and thermally unstable. Similar phenomenon of the thickness dependence has also been observed by Kawamura. In their experiment, the TiN film deposited by the conventional magnetron sputtering method was observed continuous only for the thickness above 5 nm [11]. The study on the effect of thermal treatment on the electrical properties of FAP-deposited TiN films indicates that the agglomeration and oxidation occur easily for the film with smaller thickness. This is consistent with our TCR measurement results that S1 underwent a large resistance increase as early as near 475 K (∼200 °C) but for S4, a large resistance increase only happens around 500 °C. TiN film annealed under appropriate annealing temperature exhibited better electrical properties stability because of curing the defects in film. All films underwent obvious color change against different annealing temperature due to either reduced thickness or oxidation reaction. To stabilize the electrical properties of TiN film, choosing the appropriate annealing conditions is significant.

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