Journal of Ceramic Processing Research. Vol. 10, No. 1, pp. 49~53 (2009)

J O U R N A L O F
Ceramic Processing Research

Structure and mechanical properties of titanium nitride thin films grown by reactive pulsed laser deposition

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Titanium nitride (TiN) thin films as a hard coating were grown on a Si (100) as a substrate by reactive pulsed laser deposition (reactive PLD). To investigate the effect of substrate temperature and the pressure of nitrogen (N_2) gas on the structural and mechanical properties of the as-grown TiN thin films, we varied the substrate temperature and working pressure during the deposition process. X-ray diffraction (XRD) measurements showed that the as-grown TiN thin films at 10^{-3} torr (13×10^{-2} Pa) and 450 °C grew preferentially in the direction of the (111) plane. Nano-indentation measurements showed that the hardness and elastic modulus value of the as-grown TiN thin films at 10^{-3} torr (13×10^{-2} Pa) and 450 °C were higher than with other deposition conditions. In addition, the (111) texture coefficients obviously increased for the as-grown TiN thin films at 10^{-3} torr (13×10^{-2} Pa) and 450 °C, as compared with as-grown TiN thin films with other deposition conditions; generally, an increase of the (111) texture coefficient resulted in an increase of the hardness. A field emission scanning electron microscope (FESEM) study of microstructural measurements showed that a dense columnar structure was observed with a high (111) texture coefficient while a granular structure was observed at the other deposition condition. A correlation of the reactive pulsed laser deposition parameters with the structural and mechanical properties of as-grown TiN thin films is discussed in this paper.

Key words: Reactive pulsed laser deposition, Titanium nitride, Hardness, Elastic modulus, nano-indentation.

Introduction

Titanium nitride (TiN) coatings have found numerous applications in view of their excellent corrosion and erosion resistance, relative inertness, high sublimation temperature, high hardness and desirable optical and electronic properties. Some of these applications include diffusion barriers in microelectronic devices [1], for cosmetic gold-colored purposes [2], and wave length-selective transparent optical films [3]. Specifically, in order to improve the performance and extend the life of a cutting tool, a TiN thin film is usually used as a protective coating for oxidation resistance [4]. For applications as cutting tools and diffusion barriers, a preferential orientation of a TiN thin film - (111) - can have a significant effect on its performance [5]. Many techniques, such as magnetron sputtering [6], reactive evaporation [7], ion-beam deposition [8], a plasma focus device [9], laser ablation [10, 11], and chemical vapor deposition [12] have been used to grow TiN thin films. However, chemical vapor deposition needs the use of high substrate temperature (in excess of 900 °C); which is not suitable for most sensitive substrates. In comparison, physical vapor deposition methods use a moderate substrate temperature (around 400-550 °C). Physical vapor deposition methods, in general, involve the deposition of titanium atoms on the substrate surface by sputtering or evaporation followed by a subsequent reaction with nitrogen at the substrate surface.

Pulsed laser deposition (PLD) has been extensively used in the last few years to produce a wide variety of materials in thin film form because of its advantages over other deposition techniques. PLD has emerged as a versatile, flexible, and economic procedure, which makes it possible to obtain high quality films of virtually any desired compound [13-15]. In the PLD technique, a pulsed laser beam is focused onto a target in order to evaporate its surface layers under a vacuum or low pressure process gas conditions [16]. The vaporized material consisting of atoms, ions, and atomic clusters is grown onto the substrate. When PLD is carried out in the atmosphere of a chemically reactive gas (a process known as reactive PLD), the flux of laser-ablated material interacts with the gas molecules all along the transit from the target to the substrate [17]. We describe the use of reactive PLD for the deposition of TiN thin films on silicon at substrate temperatures ranging from 25 (room temperature) to 600 °C with varying

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the working pressure from 10^{-4} torr (13×10^{-3} Pa) to 10^{-1} torr (13 Pa). In this paper, a detailed evaluation of the mechanical and structural properties of TiN thin films prepared under a wide range of conditions by the reactive PLD technique is presented.

Experimental Details

A reactive PLD system was utilized to make TiN thin films. A pulsed Nd:Yag laser (wavelength 355 nm, pulse duration 6 ns, energy 0.2 J/pulse, repetition rate 10 Hz) was used to ablate atoms from a Ti target. The beam was focused onto the Ti target by a fused silica lens. The beam diameter was 3 mm on the target. The incident angle of the beam was 45°. The target holder was rotated at a rate of 10 r/minute to reduce drilling. A blue colored plasma plume could be observed through a side view port of the vacuum chamber. All substrates were cleaned by an ultrasonic system for 20 minute in a bath of acetone and IPA. A precleaned Si (100) substrate was placed 4 cm from the target in the deposition chamber. The size of Si was the $10 \times 10\ mm^2$. High vacuum in the deposition chamber was achieved by use of a turbomocular pump. The high-purity nitrogen gas (99.995%) was introduced into the chamber through a mass flow controller. The base pressure before laser ablation was 5×10^{-6} torr (6.6×10^{-3} Pa) and the working pressure during laser ablation ranged from 10^{-4} torr (13×10^{-3} Pa) to 10^{-1} torr (13 Pa). The substrate heater was controlled by a temperature PID (proportional-integrate-derivative) controller within a few degrees K. TiN thin films were grown at various TEMPERATURES (ROOM TEMPERATURE, 300, 450, AND 600 °C). The thicknesses of these films were in the range of ~ 1 um. The deposition time for all these films was fixed to 30 minute. For the structural and texture coefficient analysis, X-ray diffraction (XRD) measurements with Cu K 1 radiation were performed. A field emission scanning electron microscope (FESEM) was used to investigate the cross section of the as-grown TiN thin films. Micro-hardness was measured by a Nano Indenter™ II (Nano Instruments Inc., Knoxville, TN). The indentation was measured in depth down to 300 nm at a displacement rate of 2 nm/s. The resolution of load and displacement of this device is 50 nN and 0.04 nm, respectively.

Results And Discussion

The XRD results of as-grown TiN thin films at room temperature, 300, 450, and 600 °C when the working pressure was fixed at 10^{-3} torr (13×10^{-2} Pa) is shown in Fig. 1 In all samples the as-grown TiN thin films showed crystalline phases. At room temperature, only a weak (111) and (200) plane were observed. The spectrum corresponding to the sample at 300 °C is characterized by the presence of peaks at $2\theta = 36.6°$, 42.7° and 61.4° (JCPDS card no.38-1420) which correspond respectively to the (111), (200) and (220) planes of TiN thin films. The as-grown

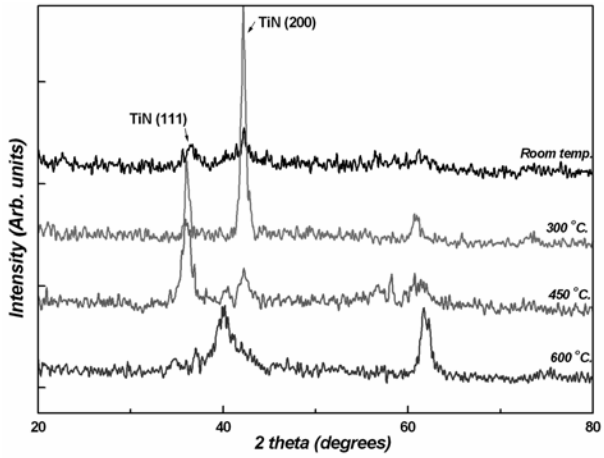

Fig. 1. X-ray diffraction patterns of TiN thin films as-grown at various substrate temperatures with 10^{-3} torr (13×10^{-2} Pa) of working pressure.

TiN thin films at 450 °C had a preferential (111) plane and a weak (200) plane. At a higher temperature, 600 °C, the (111) plane disappeared, while the peak at $2\theta = 40.1°$ and 61.4° are attributed to the diffraction from Ti (101) (JCPDS card no. 44-1294) and TiN (220) plane. Additionally, to calculate the texture coefficient of the (111) plane of the as-grown TiN thin films, we used the following equation [18]:

$$\text{Texture coefficient} = I(111) / \{ I(111) + I(200) \}$$

where, I (hkl) is the integrated intensity of the corresponding Bragg peak. The texture coefficient results of TiN thin films is shown in Fig. 2 The texture coefficient of as-grown TiN thin film at 450 °C was 0.82. There values of the texture coefficient indicate a high degree of orientation in the (111) direction. On the other hand, the TiN thin film as-grown at 600 °C had a texture coefficient of 0.04. The reason was not exhibited

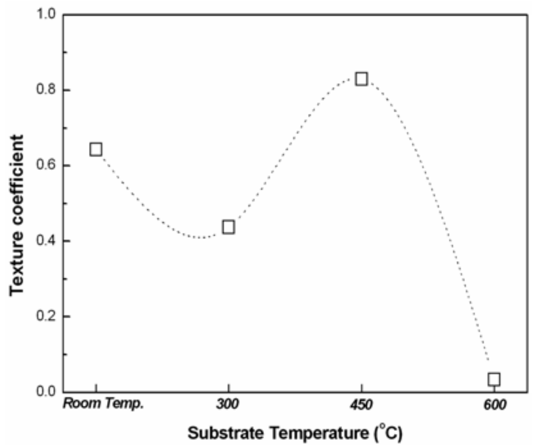

Fig. 2. Texture coefficient of the TiN thin films as a function of substrate temperature with 10^{-3} torr (13×10^{-2} Pa) of working pressure.

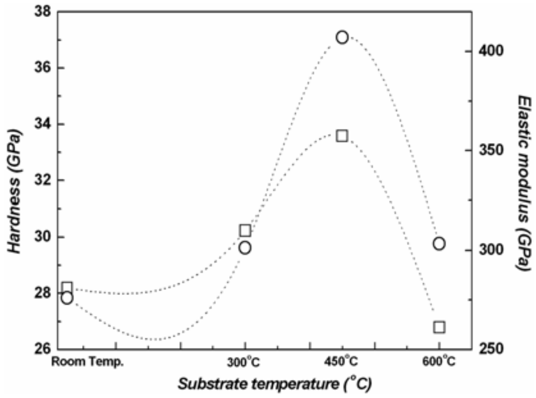

Fig. 3. Hardness (□) and elastic modulus (○) at a displacement 100 nm of TiN thin films as-grown at various substrate temperatures with 10^{-3} torr (13×10^{-2} Pa) of working pressure.

in the crystalline TiN phase. To confirm hardness (H) and elastic modulus (E) of the TiN thin films grown at room temperatures, 300, 450, and 600 °C with 10^{-3} torr (13×10^{-2} Pa) of nitrogen pressure, we examined the nano-indentation measurements shown in Fig. 3 The hardness and elastic modulus of TiN thin films can be taken at the indentation displacement of 100 nm and are tabulated in Table 1. As the substrate temperature is increased from room temperature to 450 °C, the hardness and the elastic modulus also increase. With a further increase of the substrate temperature, both H and E values are decreased. At 450 °C, the hardness and the elastic modulus are shown to be the maximum values of 33.58 and 407.12 GPa, respectively. The TiN thin film prepared at 450 °C also shows the highest texture coefficient value. As a result, the hardness and elastic modulus of the as-grown TiN thin film depended on the degree of (111) preferential orientation. This result agrees well with research reports [18] showing that TiN thin film hardness increases with an increase in the (111) texture coefficient.

Table 1. Hardness and elastic modulus of the TiN thin films prepared using different deposition condition parameters

Substrate Temp. (°C)	N_2 Pressure (torr)	Hardness (GPa)	Elastic Modulus (GPa)
Room Temp	10^{-3} (13×10^{-2} Pa)	28.19	276.10
300	10^{-3} (13×10^{-2} Pa)	30.23	301.37
450	10^{-3} (13×10^{-2} Pa)	33.58	407.12
600	10^{-3} (13×10^{-2} Pa)	26.79	303.36
450	10^{-4} (13×10^{-3} Pa)	32.91	363.98
450	10^{-2} (13×10^{-1} Pa)	24.32	291.05
450	10^{-1} (13 Pa)	22.12	276.25

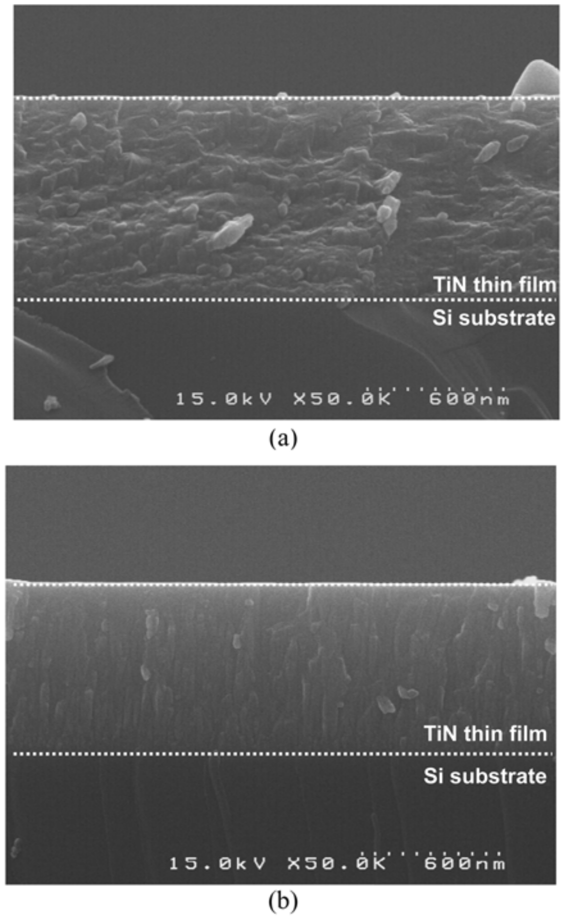

Fig. 4. Field emission SEM micrographs of cross sections at substrate temperatures of TiN thin films grown by reactive PLD. (a) 600 °C, (b) 450 °C.

This is attributed to the fact that the Schmid factor of all slip systems is 0 if the applied load is in a <111> direction on the (111) plane, and this increases the hardness of TiN thin film [19]. Fig. 4 shows the FESEM cross sections for the as-grown TiN thin films. The TiN thin film prepared at 450 °C shows a dense columnar structure but the film at 600 °C shows a granular structure. The FESEM results shows that a high hardness value has a columnar structure of as-grown TiN thin film.

X-ray diffraction scans and texture coefficients obtained for TiN thin films as-grown at the substrate temperature of 450 °C with the N_2 pressure varied from 10^{-4} (13×10^{-3} Pa) to 10^{-1} torr (13 Pa) are shown in Fig. 5 and 6, respectively. Also the average values of H and E taken at a displacement of 100 nm are presented in Fig. 7 The films grown at a low working pressure (lower than 10^{-3} torr (13×10^{-2} Pa)) have a (111) peak and a hardness higher than 32 GPa. In the case of the films grown at a high working pressure (higher than 10^{-2} torr (13×10^{-1} Pa)), the hardness shown is lower (lower than 28 GPa) and a (111) peak is not shown in the XRD pattern. These hardness values are considered to be 30% higher than those for TiN thin films prepared by non-reactive PLD [20]. which were

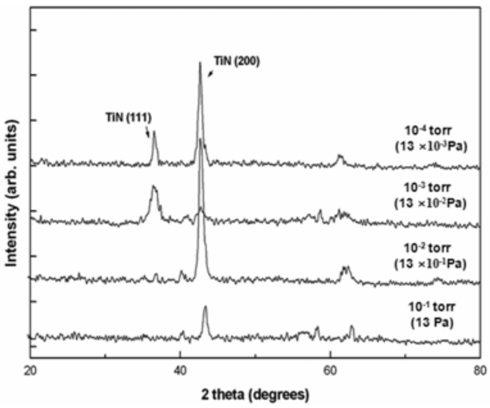

Fig. 5. X-ray diffraction patterns of TiN thin films as-grwon at various working pressures with 450 °C as the substrate temperature.

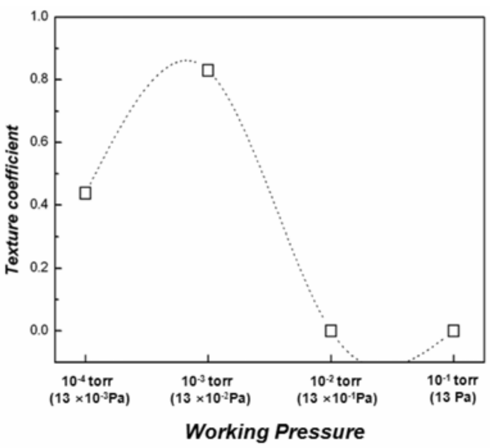

Fig. 6. Texture coefficient of TiN thin films as a function of working pressure with 450 °C as the substrate temperature.

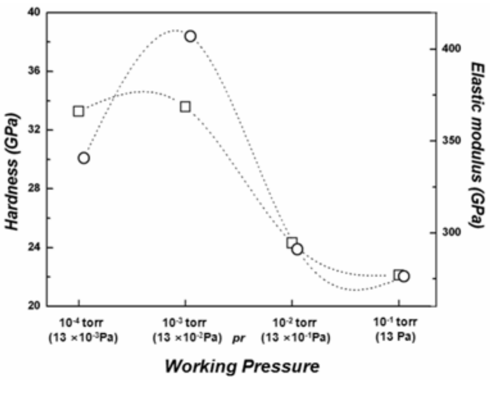

Fig. 7. Hardness (□) and elastic modulus (○) at displacement 100 nm of TiN thin films as-grown at various working pressure with 450 °C of substrate temperature.

prepared using a TiN target instead of a Ti target without N_2 gas in a vacuum chamber. This indicates that reactive PLD can improve the mechanical properties of the film significantly compared to that of the a grown with non-reactive PLD. This result agrees well with the texture coefficient calculated results. Fig. 8 shows the FESEM

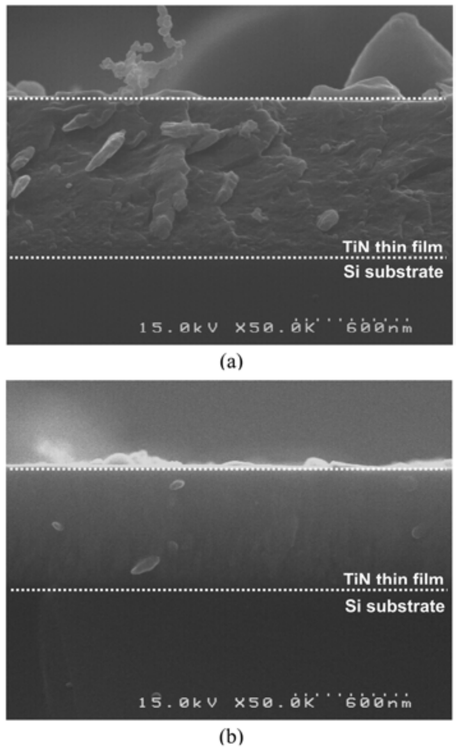

Fig. 8. Field emission SEM micrographs of cross sections with the working pressure of TiN thin films grown by reactive PLD at (a) 10^{-1} torr, (b) 10^{-4} torr.

cross sections for the as-grown TiN thin films at a substrate temperature 450 °C with the working pressure varied between 10^{-4} torr (13×10^{-3} Pa) and 10^{-1} torr (13 pa). the tin thin film prepared at a working pressure of 10^{-4} torr (13×10^{-3} Pa) shows a dense columnar structure but the film at 10^{-1} torr (13 Pa) shows a granular structure.

In reactive PLD, the kinetic energy of the ablated atoms is dependent upon the ambient pressure [21]. As expected, the average kinetic energy of the ablated atoms in low working pressure is higher than that of the ablated atoms at a high working pressure. Neamtu *et. al*. [21] estimated the thermalization pressure for the Ti atoms in the ablated flux. The vapor flux is not thermalized (high kinetic energy) if the gas pressure is less than 3.5×10^{-4} torr (4.5×10^{-4} Pa). At a pressure higher than 7.5×10^{-3} torr (9.7×10^{-3} Pa), the atoms in the ablated flux are completely thermalized (low kinetic energy) at the moment of their incidence on the substrate. Oh and Je [22] investigated the TiN thin film orientation change with the energy of the bombarding particles. They reported that a (200) orientation of a TiN thin film was changed to (111) by increasing the kinetic energy of the bombarding particles. In our experiment, TiN thin films prepared at low working pressure (lower than 10^{-3} torr (13×10^{-2} Pa)) in a reactive PLD process have a (111) orientation and high hardness. However, the films prepared at a high working pressure (higher than 10^{-2} torr (13×10^{-1} Pa)) do not have a preferential (111) orientation and the hardness is low.

Conclusions

Reactive PLD was used to deposit TiN thin films on Si by varying the substrate temperature and N2 pressure. At 10^{-3} torr (13×10^{-2} Pa) working pressure, the hardness and elastic modulus of the TiN thin films were maximized when the substrate temperature was 450 °C. Also, the texture coefficient of the TiN thin film has the highest value as compared with TiN thin films grown in other deposition conditions. In the case of the TiN thin films as-grwon at a fixed substrate temperature of 450 °C, a high hardness was obtained when the working pressure was lower than 10^{-3} torr (13×10^{-2} Pa). All the films that have a preferential (111) plane peak show a high hardness (higher than 30 GPa). These results indicate that the reactive PLD of TiN thin films on Si can improve the mechanical and structural properties of the films significantly as compared to that of TiN thin films grown with non-reactive PLD.

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