Laser Ablation Synthesis and Characterization of Nitride Coatings

A. Kumar, H.L. Chan, U. Ekanayake, A. Wierzbicki, and N.B. Dahotre

Thin film nitride coatings were deposited on Si (100) substrates by the pulsed laser deposition (PLD) technique. The PLD method is a unique process for depositing high quality thin films with novel microstructure and properties. Boron nitride (BN) films deposited on Si (100) substrates have a higher percentage of c-BN phases when processed in higher nitrogen partial pressure. Titanium nitride films deposited on Si (100) substrates at a higher temperature (600 °C) have better quality crystallinity and higher hardness and Young's modulus values than films deposited at lower temperatures. Nanoindentation technique was used to measure the mechanical properties of thin films. The film orientation was determined by x-ray diffraction. Atomic force microscopy (AFM) technique was used to understand the growth structure of the films.

Keywords boron nitride, hardness, modulus, pulsed laser deposition, titanium nitride

1. Introduction

Hardness is an important material property for films utilized in electronic, optical, and mechanically functional applications. Traditionally, the term "hard coating" refers to the property of high hardness in the mechanical sense with good tribological properties. The coatings of transition metal nitrides have numerous applications in mechanics and microelectronics due to their hardness, good conductivity, and chemical stability (Ref 1).

Cubic boron nitride (c-BN) films possess properties comparable to that of diamond in terms of thermal conductivity, chemical inertness, electrical resistivity, optical band gap, and mechanical hardness. Therefore, they are becoming competitive candidates in the field of optical, electrical, and hard coating applications (Ref 2). Several methods were used to prepare c-BN films including ion-assisted evaporation, radio frequency (rf) sputtering, microwave plasma chemical vapor deposition (CVD), and electron cyclotron resonance plasma CVD. The growth of polycrystalline c-BN by CVD usually requires very high substrate temperatures (900 °C), but c-BN can be grown by pulsed laser deposition at low substrate temperatures. Although different deposition methods are available, the content of c-BN phase is less than 80% in the films (Ref 2-4).

Interest in titanium nitride (TiN) film is based on its unique combination of chemical inertness, high thermal and electrical conductivity, high melting point, thermodynamic stability, low mass diffusivity, excellent wear resistance, and beautifully lustrous color (Ref 5-7). The broad potential range of applications resulted in development of a wide variety of techniques for TiN films. These deposition techniques include most physical vapor deposition (PVD) and CVD techniques. In this context, the PLD method was utilized to form high quality TiN thin films on Si (100) substrates at low temperatures.

A. Kumar, H.L Chan, U. Ekanayake, and **A. Wierzbicki,** University of South Alabama, Mobile, AL, USA; **N.B. Dahotre,** University of Tennessee Space Institute, Tullahoma, TN, USA.

In the last decade, the PLD method emerged as an excellent technique for the deposition of superhard coating thin films (Ref 8-11). The benefits of using PLD are high reaction rate of nitride formation under nonequilibrium conditions. Furthermore, it has the advantages of improving adhesion to the substrate, ease of control of composition and thickness of the film, and the possibility of synthesizing compound films and growing films at room temperature. The goal of this research is to understand the structure-property relationship in thin film deposited by laser ablation.

2. Experimental

The PLD system at the University of South Alabama consists of a laser, a six-way cross vacuum chamber, vacuum pumps (rotary vane and turbo molecular vacuum pumps), and other relevant instrumentation. A PLD system is capable of depositing multilayer structures composed of five different materials, in a vacuum of 10^{-8} torr at 700 °C, with a background atmosphere of nitrogen, argon, and oxygen. Figure 1 is a schematic diagram of a PLD system. A high-energy pulsed laser beam is directed onto the target materials for deposition of thin films inside the experimental chamber. The silicon substrates were cleaned ultrasonically with trichloroethylyne, acetone, and methanol and then etched in a 20% hardenability factor (HF) solution prior to loading inside the chamber. The boron nitride (BN), TiN films were deposited on Si (100) substrates at different temperatures varying from room temperature to 600 °C. Structural parameters were measured using x-ray diffraction (XRD) (Rigaku DMAX, Danvers, MA; with thin film attachment).

Atomic force microscopy, constant force, and contact mode (Nanoscope III, Digital Instruments) were used to obtain all images. Tips were pyramidal silicon nitride. Using this method, the samples were attached to steel pucks (12 mm diam), which were held on a piezoelectric scanner. The scanner moves the sample in a raster motion under the tip, which is maintained via a feedback loop in a constant position. The movement of the piezo, which is required to hold the tip in place as the sample is rastered underneath, is used to construct an image of the surface topography.

The mechanical properties (hardness and modulus) of the films were measured using a Nano Indenter IIA (Nano Instruments Inc., Knoxville, TN). A diamond tip with a known geometry is forced into the material. This indentation depth yields the area of contact between the indenter and the material. The hardness and modulus of the device can be determined at each point. The indentation is performed with a controlled force and continuous monitoring and recording of the displacement of

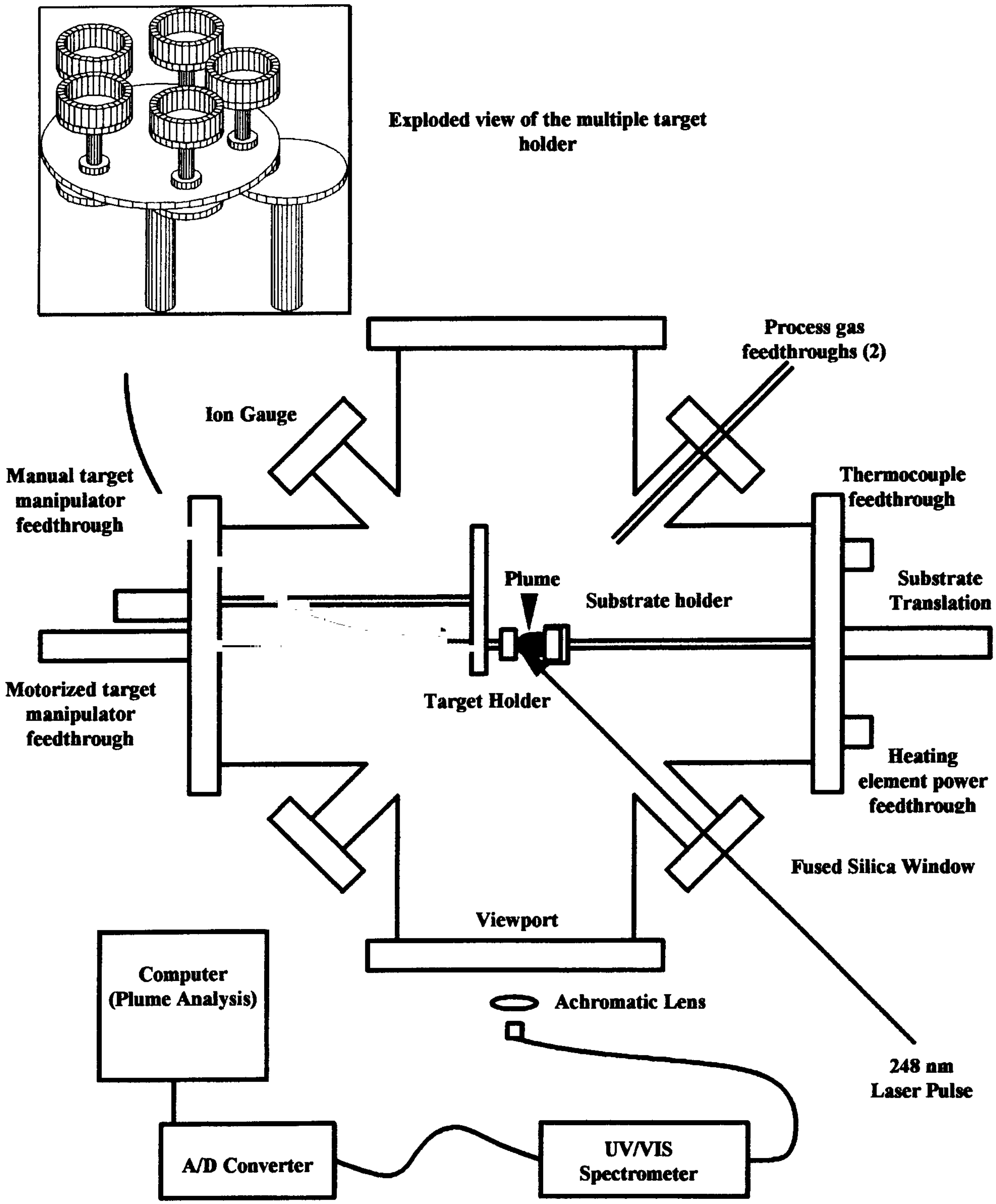

Fig. 1 Schematic diagram of the pulsed laser deposition system at the University of South Alabama

the indenter. Analysis of the load-displacement curves provides information on the hardness and the elastic and creep properties of the films.

3. Results and Discussion

3.1 *Boron Nitride Coating*

In this study, BN films were deposited on Si (100) substrates with varying temperatures (100 to 600 °C) and partial pressures of N_2 (100 to 400 mtorr). Preliminary optical observation indicates a bluish color and very smooth surface for the c-BN deposited under different conditions. The optical observation revealed a clean featureless surface, with only a small amount of particulate detected on the film, which is the characteristic feature of the laser deposition process.

Figure 2 shows the BN bonding characteristics of the films on Si (100) at 400 mtorr with varying temperatures (100, 200, 300, and 400 °C). The figure shows a small infrared (IR) peak at 800 cm^{-1} (sp^2 bonded h-BN). A strong peak is found at 1065 cm^{-1} (sp^3 bonded c-BN). The intensity of the c-BN IR spectrum is higher than the spectrum of h-BN. This clearly shows that the deposited films consisted mainly of c-BN phase and were processed in a 400 mtorr nitrogen environment.

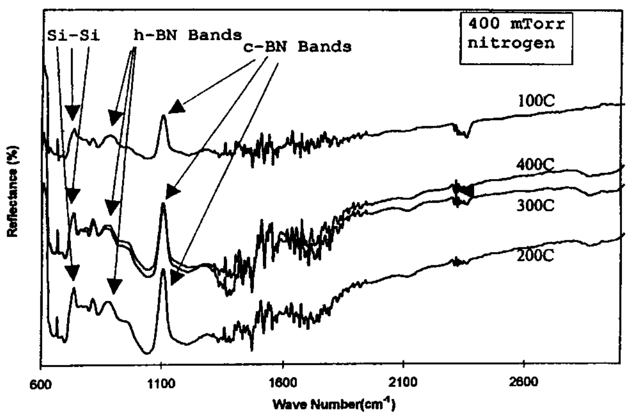

Fig. 2 Fourier transform infrared spectroscopy spectrum of boron nitride films on Si (100) at different processing temperatures in 400 mtorr nitrogen environment

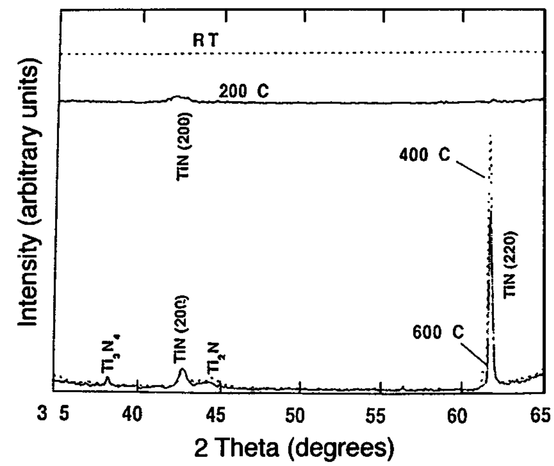

Fig. 3 X-ray diffraction results of TiN films deposited on Si (100) substrates at different temperatures

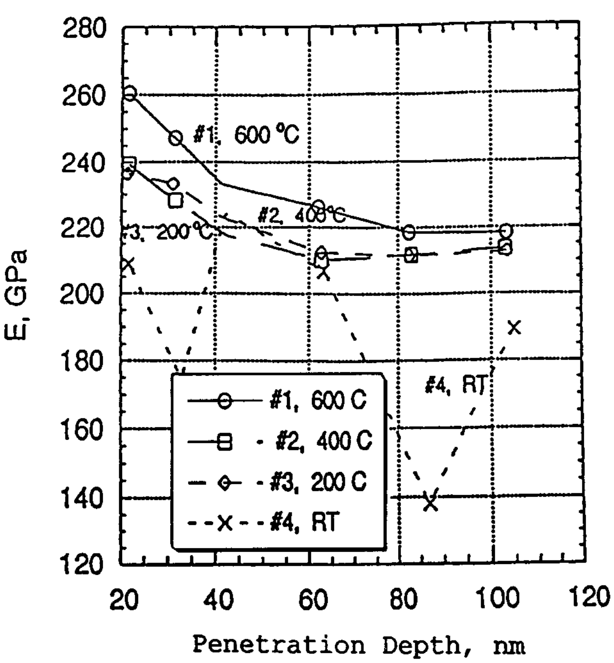

Fig. 4 Young's modulus of TiN on Si (100) substrates as a function of penetration depth

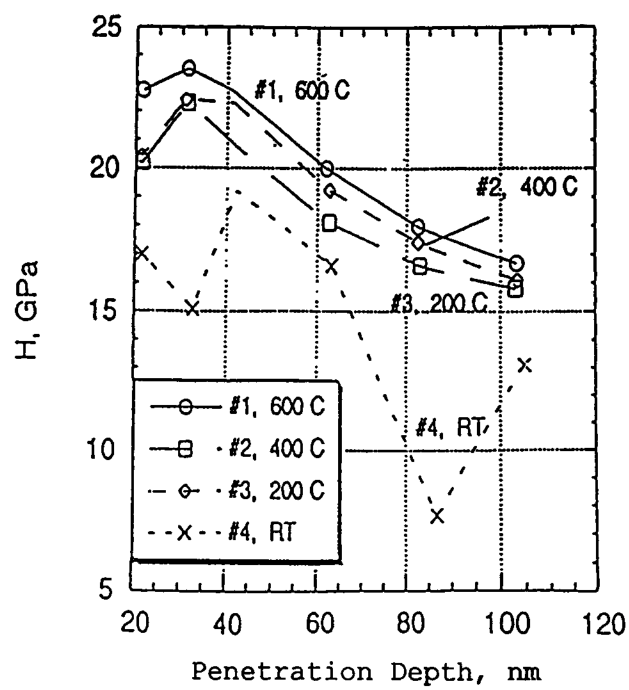

Fig. 5 Hardness of TiN films on Si (100) substrates as a function of penetration depth

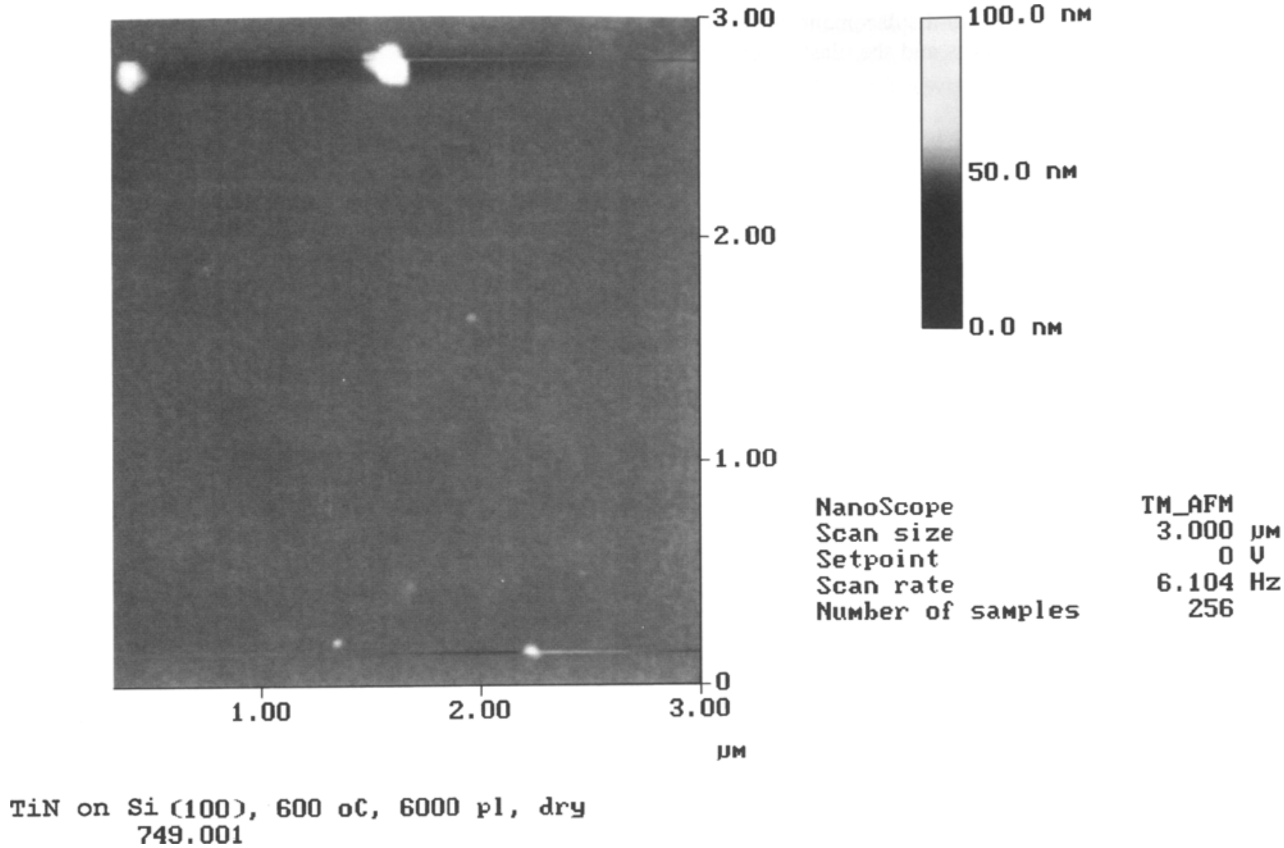

Fig. 6 Atomic force microscopy micrograph of TiN films deposited at 600 °C

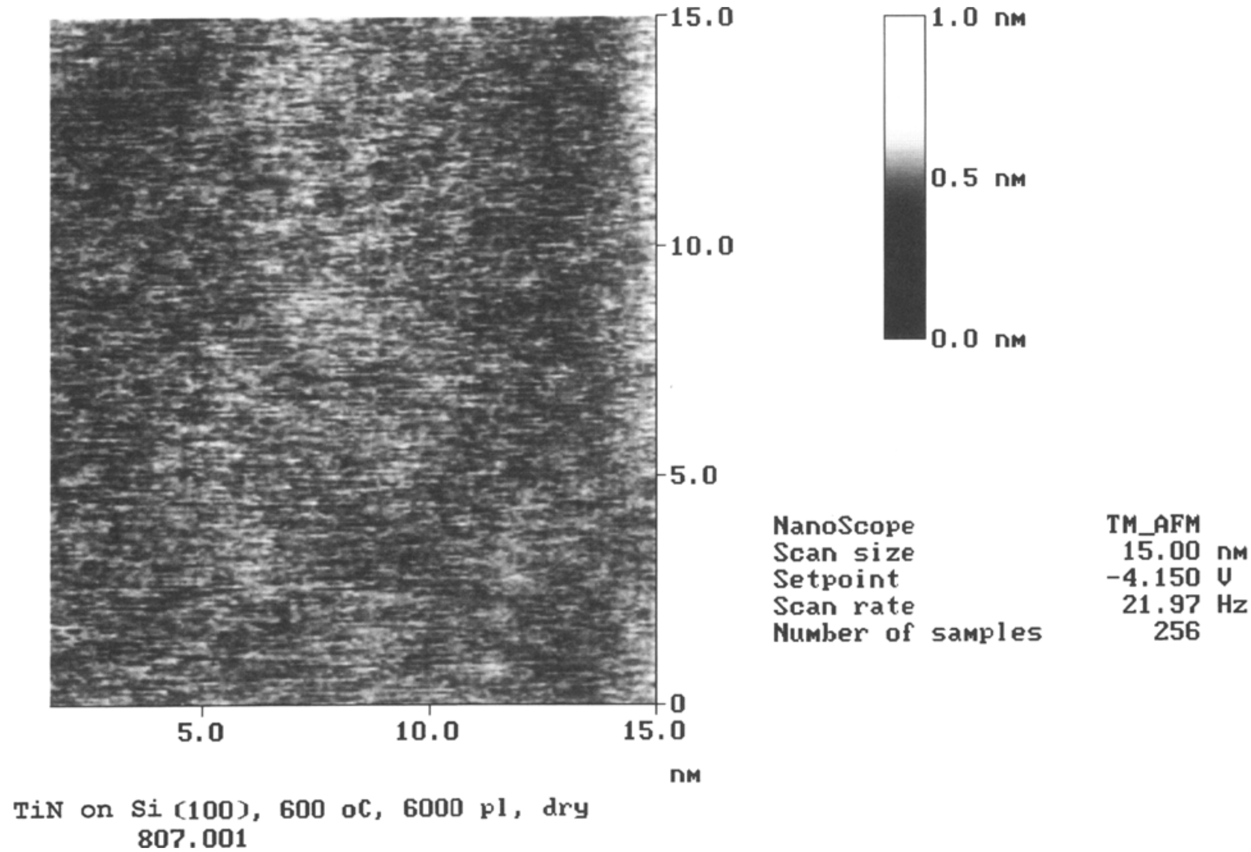

Fig. 7 Atomic force microscopy micrograph of TiN films deposited at 600 °C. The scan area size is 3 by 3 µm.

3.2 *Titanium Nitride Coating*

The film structure of TiN films, deposited at room temperature, 200, 300, 400, and 600 °C on Si (100) substrates, was found to be strongly dependent on the substrate temperature. The x-ray diffraction (XRD) results in Fig. 3 show only one broad diffraction peak at the lower substrate temperature. The peak can be indexed to a (200) textured TiN phase. The grain size of these films is in the nanocrystalline range. At room temperature, the film quality and film adhesion were low. At higher substrate temperatures (400 and 600 °C), the films were crystalline and contained multiple phases. The crystallographic orientation of TiN grains also changes to a (220) orientation. The sharp diffraction peaks indicate that the grain size of the films is substantially larger. The variation of elastic modulus and the hardness of TiN film deposited at room temperature, 200, 300, 400, and 600 °C, as a function of indenter displacement, are presented in Fig. 4 and 5, respectively.

Both properties appear to approach the values corresponding to that of Si (100) substrate at greater penetrations. The hardness of a variety of metallic and ceramic films was found to be substantially lower at penetrations of 20 nm. Therefore, it is suggested that the modulus and the hardness of the TiN films can be taken at the indenter penetration of 20 and 30 nm, respectively. These values are considerably higher than those obtained for reactively sputtered deposited TiN on cemented carbide and steel substrate and compare well with TiN films prepared by plasma arc method (Ref 12) on Si (100). The discrete variation of hardness and modulus of TiN films deposited at room temperature was probably due to the poor film quality.

Figures 6 through 8 show the atomic force microscopy (AFM) results of TiN films on Si (100) substrate at 600 °C. The quality of the film is smooth with only a few particles present on the surface (Fig. 6). Figure 7 shows the AFM micrograph of TiN films deposited at 600 °C at the scan area of 3 by 3 μm. The film quality is dense and has uniform coverage throughout the surface. Figure 8 shows the lattice imaging of the same TiN films deposited at 600 °C at the scan area of 15 by 15 nm. The image of Fig. 8 was processed by applying the autocovariance function. This clearly shows that the lattices of the films are highly oriented, and the distance between the two lattice points is very close to the lattice parameter of TiN.

4. Conclusions

The PLD technique was utilized to fabricate excellent quality thin films of nitride coating materials. In the case of BN films processed by PLD on Si (100) substrates, the Fourier transform infrared spectroscopy (FTIR) results show mostly c-BN bonds in all films. Boron nitride films on Si (100) have a higher intensity of c-BN (sp^3 bonded) spectrum compared to

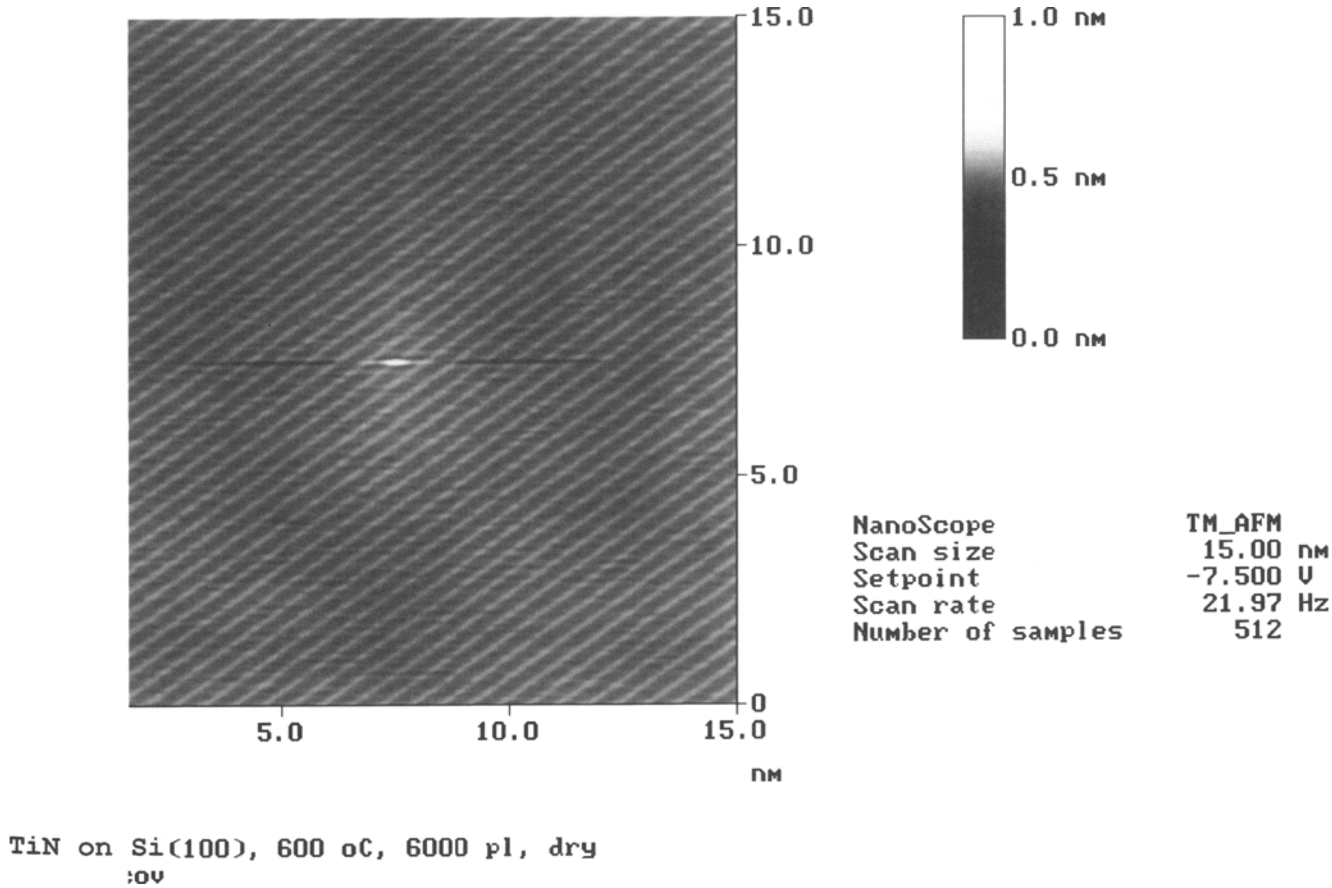

Fig. 8 Atomic force microscopy micrograph of TiN films deposited at 600 °C showing lattice imaging of films. The scan area size is 15 by 15 nm.

the h-BN structure (sp^2 bonded). It was also found that the BN films have a higher percentage of c-BN phase during deposition at high nitrogen partial pressure. The TiN films deposited at 600 °C have better quality crystallinity and higher hardness and modulus values than films deposited at lower temperatures.

Acknowledgments

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