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ABSTRACT

The pulsed-laser deposition technique has been used to form thin films of TiN on (100)-oriented single crystal substrates of silicon and rocksalt. Using atomic force microscopy, it was revealed that TiN films grown on silicon at substrate temperatures ranging from 50°C to 500°C were extremely smooth—the mean roughness being ~ 0.2 nm. Thin TiN films deposited on freshly cleaved NaCl were found to be epitaxial at substrate temperatures as low as 50°C. Epitaxy in this latter system is believed to be due to the structural similarity between film and substrate and the almost exact 4:3 coincident site lattice.

INTRODUCTION

With excellent mechanical, thermal, and electronic properties, such as good thermal stability, high corrosion resistance, and low electrical resistivity, titanium nitride (TiN) thin films have many applications ranging from coatings on cutting tools to diffusion barriers in VLSI microelectronics. This broad range of applications has resulted in the development of a wide variety of deposition techniques to form TiN films. These techniques include both physical and chemical vapor deposition methods. However, most of these techniques require moderate to high substrate temperatures to form oriented crystalline films. The high deposition temperature inhibits the use of TiN films in some applications where the substrate cannot withstand elevated temperatures. It is therefore of interest to study the possibility of TiN deposition at lower substrate temperatures.

The major obstacle to low temperature growth is the difficulty of obtaining the high surface mobility required for the nucleation and growth of crystalline or epitaxial films at low substrate temperatures. This limitation can be overcome by delivering the material to the substrate in unique chemical forms (e.g., clusters or reactive species), in charged or highly excited states, and/or with appreciable kinetic energy. The latter objective may be accomplished by the use of pulsed-laser deposition (PLD). In PLD, a focused high-power excimer laser is directed towards a target in a high-vacuum chamber. The strong laser-target interaction results in the formation of a high temperature, high velocity, and electronically excited plasma consisting of neutral atoms, molecules, ions, and electrons. With little loss of energy in high vacuum, the plasma is transported to and deposited onto a substrate.

Several groups have reported the formation of TiN thin films by PLD using irradiation of either metallic targets in a nitriding atmosphere [1,2] or stoichiometric nitride targets [1,3,4]. Even when the substrate is maintained at room temperature during film deposition, crystalline TiN films have been formed on silicon [3]. Narayan and co-workers have reported the formation of single crystal TiN films on silicon substrates heated during deposition to temperatures in the range 600 - 700°C [4]. This latter result is unusual given the relatively large lattice mismatch (25%) between Si (a_0 = 0.543 nm) and TiN (a_0 = 0.422 nm). The cube-on-cube epitaxy appears to be enhanced by the 4:3 near-coincident site lattice where the mismatch is less than 4%.

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EXPERIMENTAL

Titanium nitride films were formed by focusing a Lambda Physik EMG203 excimer laser operating on KrF (λ = 248 nm) onto a hot-pressed TiN target supplied by Target Materials Inc. The laser fluence was 4 J/cm^2, the pulse duration was 20 ns, and the pulse repetition rate was in the range 4 to 8 Hz. The films were deposited in vacuum (base pressure 10^{-6} torr). Two types of substrate material were used in the present study: (100)-oriented single crystal silicon and rocksalt. (No attempt was made to remove the native oxide layer on the silicon substrates.) The substrates were mechanically clamped onto the stainless steel plate of a small resistive heater and were positioned parallel to the target. The distance between the target surface and the substrate was ~ 5 cm. The temperature of the substrate heater was monitored by a thermocouple embedded into the heater block at a position just behind the substrate. All the temperatures reported here are those of the substrate heater as measured by the thermocouple.

The rocksalt substrates were used to facilitate sample preparation for transmission electron microscopy (TEM) and for parallel electron energy loss spectrometry (PEELS). Thin (~10 to 30 nm thick) TiN films were deposited onto freshly cleaved (100)-oriented NaCl substrates. Following deposition, the NaCl was dissolved in deionized water and the film collected on a slotted 400 mesh copper grid and dried in air. This specimen preparation method produces excellent samples for PEELS analysis—they are thin and of a uniform thickness. All the films were analyzed either immediately after deposition or after being stored in a desiccator for a few days. A Hitachi H600 TEM operated at 100 kV was used to examine the films. PEELS was performed with a Philips EM400T/FEG analytical electron microscope operated at 100 kV.

The surface morphology of the films was characterized with a Digital Instruments Nanoscope III Multimode atomic force microscope (AFM) operated in either contact mode or tapping mode. The images shown here are top view images with linear gray scale encoding of the height of features. The films were also examined using a JEOL JSM 6400 scanning electron microscope (SEM) operated at 20 kV. No conductive coating was applied to the samples prior to SEM analysis.

RESULTS AND DISCUSSION

The first obvious feature of all the films grown in this study was their golden-yellow color, which is characteristic of TiN [5]. The surfaces of the films were fairly free of the ubiquitous particulates associated with films formed by PLD. The occurrence of particulates on the film surface is highly dependent on the nature of the target [1]. TiN films formed from the ablation of titanium may have large spherical particles on the surface as a result of the ejection of molten metal from the target [2]. Films made from pre-formed TiN targets often show a lower number of particulates [1].

Examination of the surface morphology of the films by AFM showed that they were extremely smooth for all the substrate temperatures used in this study. Figure 1 shows AFM images of the surface of a silicon substrate and of TiN films grown at three substrate temperatures. Mean roughness values determined by the AFM software for the TiN films varied from 0.18 nm for films deposited at a substrate temperature of 500°C to 0.27 nm for films deposited at 50°C. These values can be compared to the mean roughness of 0.19 nm determined for the uncoated silicon wafer.

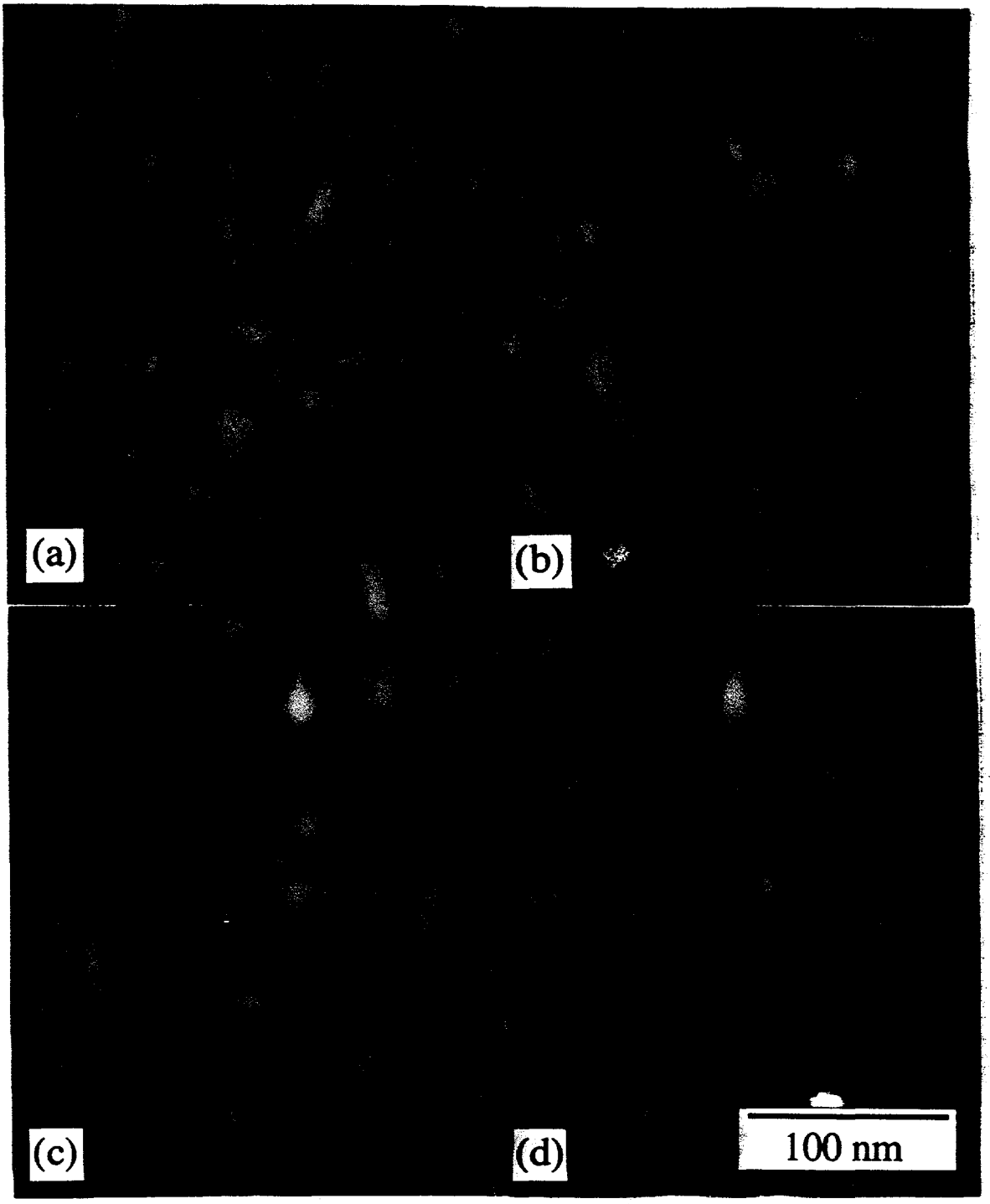

Figure 1. The surface morphology of (a) (100)-oriented silicon and (b) - (d) TiN thin films deposited onto silicon substrates at temperatures of (b) 50°C, (c) 300°C, and (d) 500°C. The z-range is 3 nm in all the images.

Figure 2 shows a series of X-ray diffraction patterns obtained from TiN thin films deposited on (100)-oriented silicon substrates at different temperatures. At a substrate temperature of 50°C, no strong diffraction maxima are observed. For films deposited at substrate temperatures of 300°C and 500°C sharp peaks in the patterns corresponding to diffraction from the (200) planes of TiN are observed indicating that these films are textured. Several groups have reported that TiN

films on silicon are oriented with the [100] of TiN parallel to the [100] of Si [1,4]. Recent results on TiN films prepared by reactive rf magnetron sputtering indicate that the preferred film orientation changes from (200) to (111) with increasing film thickness [6].

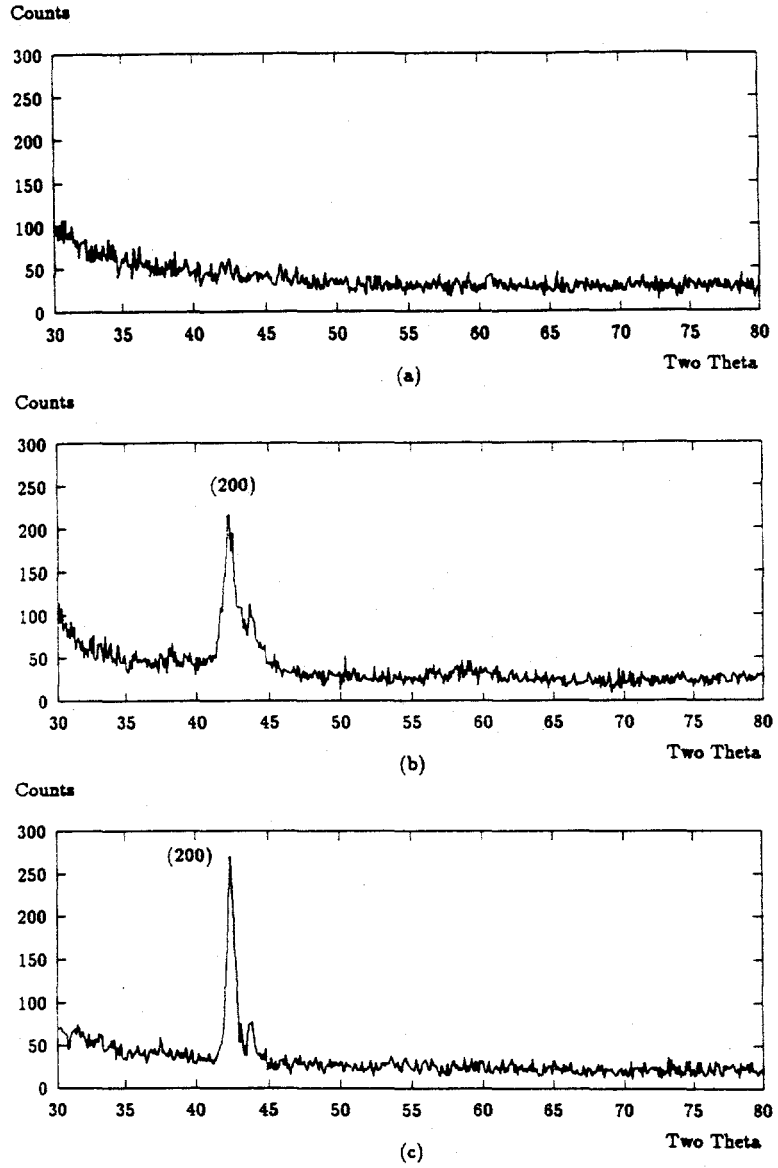

Figure 2. X-ray diffraction patterns recorded from TiN thin films deposited on (100)-oriented Si substrates at substrate temperatures of (a) 50°C, (b) 300°C, and (c) 500°C.

Electron channeling patterns (ECP), shown in Figure 3, obtained from very thin TiN films deposited on silicon at a substrate temperature of 300°C indicate that the films are highly ordered, at this stage of growth, in the film-substrate interface plane. No clear channelling patterns were acquired from thicker TiN films deposited under equivalent conditions.

Figures 4a and 4b show selected area electron diffraction (SAED) patterns recorded from free-standing thin TiN films deposited on NaCl substrates heated to room temperature and 50°C, respectively. At room temperature the TiN film is crystalline and highly textured. At 50°C the SAED patterns showed only discrete reflections which could be indexed to TiN, indicating that film growth is epitaxial on NaCl at this temperature. SAED patterns obtained from films deposited at higher temperatures all appeared identical to Fig. 4b. This result may at first be surprising

because of the large lattice mismatch (29%) between TiN and NaCl (a_0 = 0.564 nm). However, there exists an almost exact 4:3 coincident site lattice (where 4 unit cells of TiN match with three unit cells of NaCl) with a mismatch of only 0.2%. Thus as in the case of TiN growth on Si, domain matching appears to be an important feature in determining epitaxial growth in systems with large lattice mismatches [4]. The structural similarity between NaCl and TiN may also favor epitaxy with the TiN molecules occupying cation and anion sites on the NaCl (100) surface. This type of "auto-epitaxial" system can lead to epitaxial growth at low temperatures despite large lattice mismatches [7].

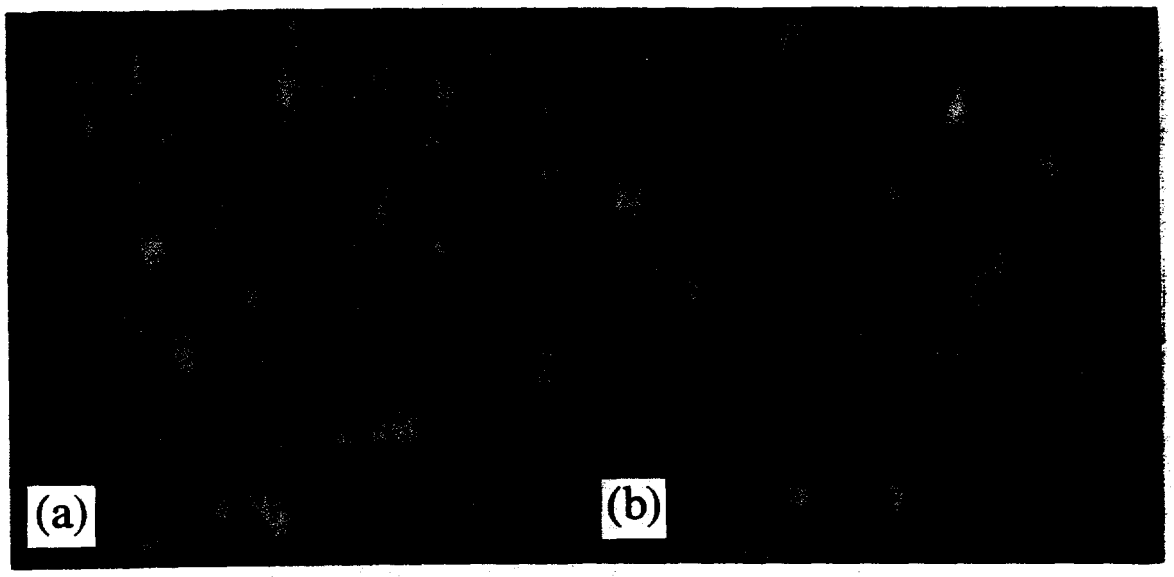

Figure 3. Electron channelling patterns recorded from (a) (100)-oriented Si and (b) a very thin TiN film deposited onto Si at a substrate temperature of 300°C.

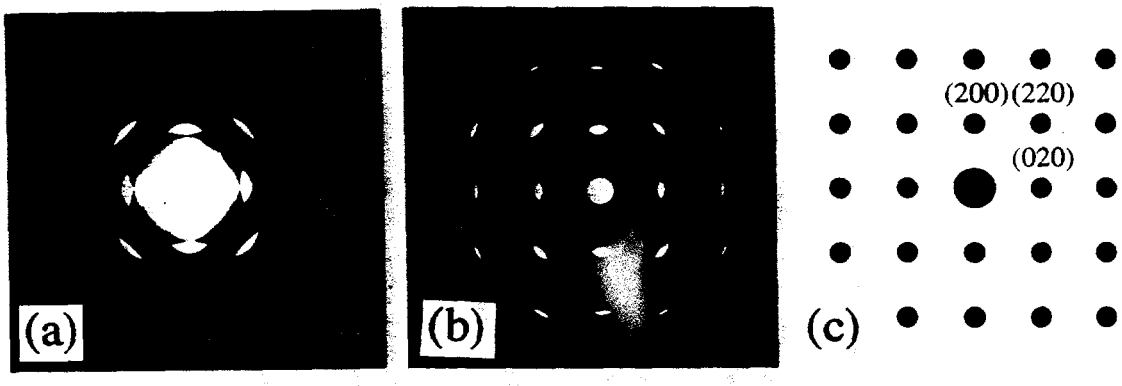

Figure 4. Selected area electron diffraction patterns from TiN thin films deposited onto NaCl substrates heated to (a) room temperature and (b) 50°C. An indexed schematic is shown in (c).

Figure 5 shows a PEELS spectrum obtained from a TiN film deposited at room temperature. The absolute composition of the films could not be determined from these spectra because there is some overlap between the Ti-L_1 edge which occurs at 564 eV and the O-K edge at 532 eV. Absolute composition determination would require multiple-least-squares analysis of second difference spectra using appropriate standards. However, relative changes in film

composition were noted from examining the jump ratios of the N-K, Ti-$L_{2,3}$, and O-K edges. The jump ratio is the ratio of the intensity at the edge-onset relative to the background intensity immediately before the edge. These ratios indicate that the amount of oxygen incorporated into the TiN films increases and the amount of nitrogen decreases when the film is grown at room temperature rather than 300°C. Oxygen contamination appears to be a frequent occurrence in TiN films. Several possible sources of this contamination have been identified [1,3].

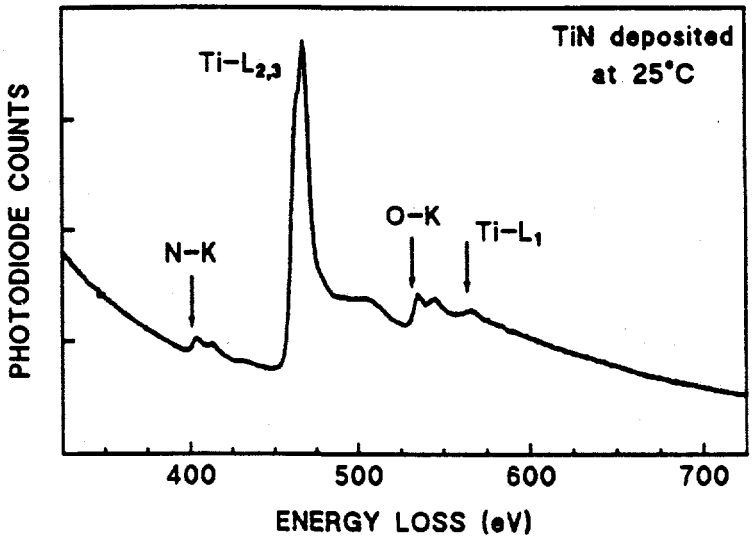

Figure 5. PEELS spectrum of TiN thin film deposited at 25°C.

CONCLUSION

In conclusion, extremely smooth oriented TiN thin films can be grown on single crystal silicon substrates by pulsed-laser deposition at relatively low substrate temperatures. Epitaxial TiN can be formed on NaCl at a substrate temperature as low as 50°C.

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