Pulsed Laser Deposition of Epitaxial Titanium Nitride on Magnesium Oxide substrate

By,

Preetam ANBUKARASU
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Under the Guidance of,

Prof. Tetsuya HASEGAWA,
Solid State Chemistry Lab,
Graduate School of Science,
University of Tokyo.
Abstract

Epitaxial layers of Titanium Nitride (TiN) deposited on Magnesium Oxide (001) by Pulsed laser deposition and the mechanism of film growth was analyzed by observing the reflection high energy electron diffraction (RHEED) pattern. The possibility of producing high quality of Titanium Nitride film at low deposition temperature was studied. Atomic force microscopy was used to observe the surface morphology of the film. The crystallinity of TiN film was studied using High resolution X-ray diffractometry and Reciprocal Space Mapping. The results indicated the formation of high quality TiN thin film. The temperature dependence on electrical resistance of the epitaxial film was studied using physical property measurement system (PPMS).

Introduction

Titanium Nitride

Titanium Nitride is a ceramic material and it has a cubic crystal structure (Rock salt structure). The structure of TiN is shown in the fig.1. Titanium Nitride has many interesting mechanical and electrical properties. It has high temperature stability, high hardness and chemical inertness which are characteristic properties of any ceramic material. In addition to this, Titanium Nitride has some anomalous properties such as good electrical conductivity and thermal conductivity. It is very uncommon for a ceramic material to have good conductivity as the ceramics are bound by strong covalent bonds.

![Fig.1: Rock salt crystal structure of Titanium Nitride](image)

The interesting properties of TiN enable it to be used in hard coatings, thermal barriers, bio-inert coatings, etc. In all these applications, TiN is used in polycrystalline form. Single crystal thin films (Epitaxial films) of TiN can have many potential applications in electronics industry and packaging industry.
Pulsed laser Deposition

Pulsed laser deposition is a versatile technique that can be used to produce high quality epitaxial films of transition metal oxides and nitrides. It makes use of a pulsed laser source which is directed on a target, which can be a metal or a ceramic. The energy imparted by the laser on the target vaporizes it instantaneously and leads to the formation of a high energy plasma. The plasma rises and is deposited on a substrate which is maintained at an elevated temperature. The entire system is maintained in a low pressure atmosphere using vacuum chamber. The process is carried out for a period of time to produce a film having thickness in the range of nanometers.

There are a few previous researches where epitaxial Titanium Nitride was produced using pulsed laser deposition. Inumaru et al. has prepared TiN on MgO substrate using titanium as a target in a nitrogen atmosphere. The nitrogen molecules were converted into radicals by using a plasma generator. They were able to produce high quality film at high substrate temperature. The main problem with the process is the high substrate temperature, which is not suited for large throw put industrial applications. The radical generator requires high initial investment. The use of titanium as target makes the nitrogen radical generator indispensable to produce high quality epitaxial films of TiN.

The main aim of the present work is to study the possibility of preparing epitaxial films at a lower temperature without the use of nitrogen radical generator. In order to eliminate the need to use nitrogen radical generator, we decided to use titanium nitride as target material instead of metallic titanium and the deposition process was carried in vacuum. This enabled us to reduce the complexity of the entire process, as there was no need to use a radical generator and adjust gas pressure at any point during the deposition. We carried out the experiment at a range of temperatures to study the effect of temperature on the crystallinity and surface of the epitaxial film. During deposition, RHEED oscillation pattern was used to study the mechanism of thin film growth.

Atomic force microscopy (AFM) was used to study the surface of the film and HR-XRD and reciprocal space mapping was used to study the crystallinity.

Experimental

Pulsed laser deposition system used for deposition was equipped with a RHEED apparatus and a KrF eximer laser was used to produce laser (λ=248nm) with required pulse frequency. the pulse frequency for all the experiments was maintained at 10Hz and the deposition was carried out for 36,000 seconds. The pressure was maintained at 10⁻⁷ Torr, which is the base pressure of the chamber. The TiN target was made to rotate at a constant rate during deposition process. The temperature of the MgO (001) substrate was maintained at different temperatures during the deposition process. The temperature was varied from 800°C to 300°C and the quality of the thin film was studied.
Results and Discussion

Atomic Force Microscopy

The atomic force microscopy image of the MgO (001) substrate is shown in the fig. 2a. The image clearly indicated the high flatness of the substrate. The RMS roughness of the substrate was found to be about 3 nm. The fig. 2b to fig. 2d shows the surface of the thin films deposited at 700°C, 500°C and 300°C respectively. From the images, it can be clearly seen that the deposited layer is highly flat and uniform, with RMS roughness of about 1.5 nm.

Fig.2a: Mgo (001) substrate, Fig.2b: TiN film at 800°C, Fig.2c TiN film at 500°C, Fig.2d TiN film at 300°C.

The film coated at 300°C was found to have asperities, which indicate segregation of metallic titanium due to low process temperature. But the overall surface flatness (1.5 nm) was better than MgO substrate. This indicates that good quality TiN film can be deposited at low temperature.
**HR-XRD**

The crystallinity of the deposited film was analyzed using HR-XRD and RSM. The XRD pattern of the films deposited at 500°C and 300°C is shown in the fig. 3.

![XRD pattern of MgO and TiN](image)

The XRD pattern corresponding to the planes (200) and (400) clearly indicate a shoulder associated to TiN. The shoulder is observed in both the XRD patterns. The 2θ value of the shoulder also corroborates with the values that correspond to the TiN peak. The presence of such a shoulder is due to the small d-spacing difference between MgO and TiN.

The film prepared at 300°C was found to have a more pronounced shoulder than film prepared at 500°C. The sharpness of the peaks and shoulder indicate good crystallinity of the film.
The samples were analyzed further using 1D detector and reciprocal space mapping. The 1D detector can be used to resolve the shoulder more clearly. The fig. 4 shows the XRD pattern obtained using 1D detector. The peak corresponding to TiN was clearly resolved by this method.

Fig. 4: Pattern obtained using 1D XRD scan of sample processed at 300°C

Reciprocal space mapping of the sample and the substrate is shown in the fig. 5. The RSM showed the presence of highly crystalline TiN and the absence of residual stresses in the thin film.

Fig. 5: Reciprocal space mapping of the sample and the substrate
**R-T curve**

The resistance of the film with respect to temperature was determined using physical property measurement system (PPMS). The plot of resistance Vs temperature is shown in the fig.6. The plot clearly showed that TiN has a typical metal like behavior with reduction in resistance with reducing temperature.

![R-T curve](image)

**Fig.6: R-T curve**

**Conclusions**

The following conclusions were made from the experiments,

- TiN epitaxial thin film can be fabricated at low temperature on MgO substrate from TiN target using PLD.
- AFM indicated highly flat TiN. Generally, high temperature favored better surface finish.
- The TiN was characterized by XRD, which indicated the formation of crystalline TiN in all the samples.
- The resistance measurement with decreasing temperature indicated that the TiN thin film behaves like a typical metal. The resistance was found to decrease with decreasing temperature.

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