HRTEM STUDY ON TiO_2/TiNO FILM GROWN BY LP-MOCVD PROCESS.

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Transition metal nitride coatings with nanometric grain size are of particular interest due to their high hardness and strength, thermal stability, attractive appearance and chemical inertness. The improvement of tool materials coated with transition metal nitrides has led to interest in developing superhard coatings for wear protection under complex loads and aggressive environments (1). Besides, TiO_2 and TiN thin films are important materials for microelectronics, optics, and medical applications (2, 3). The interest concerning TiNO films has increased during the past few years, since the presence and the control of oxygen in titanium nitride leads to a promising functional range of materials from insulating TiO_2 to conducting TiN, whose resistivity is tunable as a function of its N/O ratio (4). In this work TiO_2/TiNO structure was grown on a Cu substrate that was cleaned in a 5% H_2SO_4 water solution and rinsed in abundant deionised water before deposition. The growth was carried out in a horizontal LP-MOCVD equipment. The deposition was performed by using $Ti(OCH(CH_3)_2)_4$ as both titanium and oxygen sources and the carrier gas was nitrogen. Ammonia (NH_3) was used as nitrogen source. Thus, the fact of adding ammonia or not during the deposition process leads either to TiNO or to TiO_2 films, without any growth breaking. The deposit was carried out at 600°C under 60 torr of pressure. The first step was to deposit a ten-minute buffer layer of TiO_2, followed by five periods of TiNO/TiO_2. The surfaces of specimens were examined in a transmission electron microscope (TEM) and the chemical composition of the film was determined by using energy dispersive analysis (EDS). Fig.1a shows the film deposited, whose average thickness is in the order of 30 nm. A high-resolution image of a nanocrystal is shown Fig. 1b. Moiré fringes are also observed. The structure is composed of nanometric grains with dimensions around 10 to 20 nm. The lattice spacing of the planes was measured to be about 3.5 Angstrons. The EDS analysis obtained from the surface of the film is shown in Fig. 2a. This surface is composed of the elements Ti and O. In Fig.2b it can be seen that nitrogen was really incorporated to the TiO_2 cell. The crystalline phase present is anatase, as it can be seen in the electron diffraction pattern shown in Fig. 3. It was not possible so far to distinguish if there are some grains of TiO_2 or TiNO in this surface. It is possible that what exist is a mixture of grains presenting a medium composition $TiO_{(2-x)}N_x$. Based on the results shown so far, it can be stated that a conventional LP-MOCVD system using $Ti(OCH(CH_3)_2)_4$ and ammonia as precursors can be used to grow mixed films in a only one step growth. More characterization studies are needed in order to verify how TiO_2 and TiNO grains are disposed in the layer.

Acknowledgements

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References

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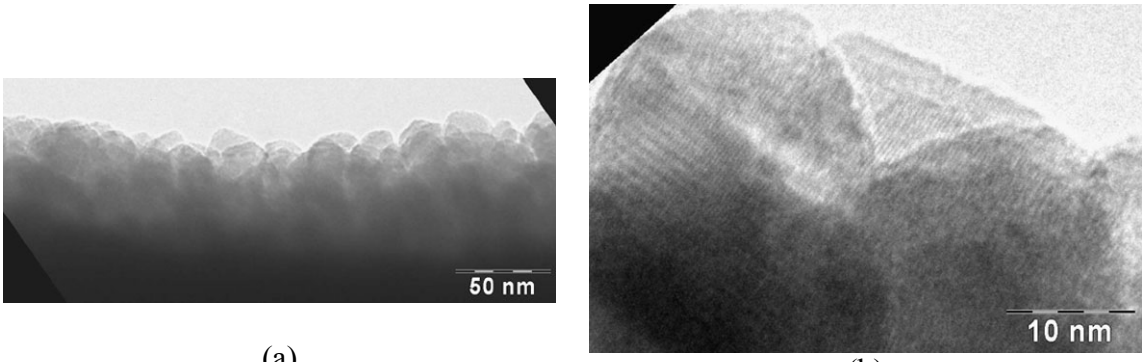
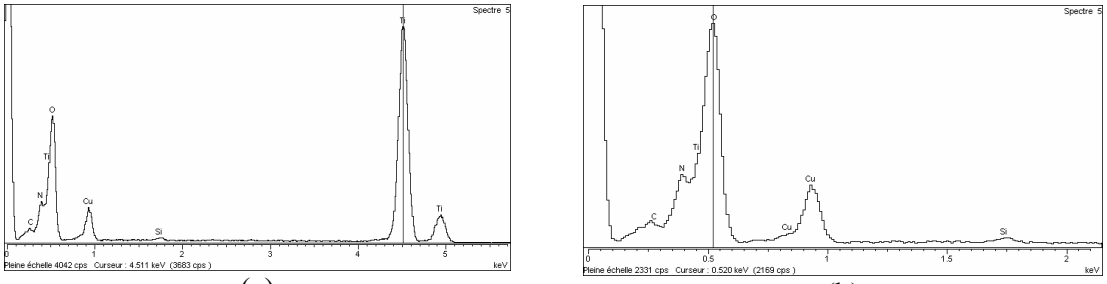


(a) (b)

Fig.1: (a) TEM bright field image of the TiO_2/TiNO film. The copper substrate appears darker. (b) High-Resolution image of a nanocrystal showing lattice planes.



(a) (b)

Fig.2: EDS spectrum from the film. (a) general view; (b) magnification on the low energy range.

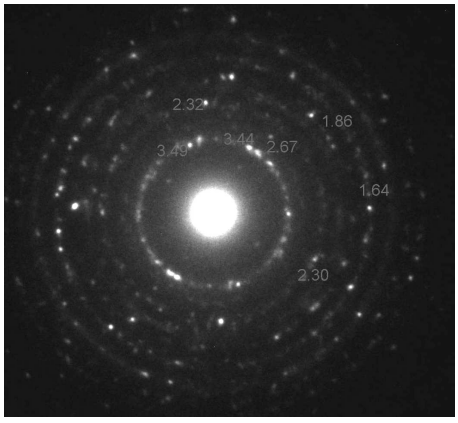


Fig.3: Selected area electron diffraction pattern of the TiO_2/TiNO film. Some interplanar spacings (given in Angstrons) are measured from the main spots.