Characterization of Titanium Compound Films Deposited by Plasma-CVD

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Titanium compound films (Ti-N, Ti-C, Ti-C-N, Ti-N-O, Ti-C-O etc.) have been much interested in recent years because of their chemical stability, high hardness, high abrasive resistance and decorative coloration [1-3]. Fundamental informations on these films have not been obtained sufficiently, however, except some investigations. In the present study, the authors characterized titanium compound film using SEM, XRD, SIMS and XPS. Titanium compound film was prepared on the SUS 316 stainless steel substrate by R.F. plasma-CVD using a mixture of $TiCl_4$ (99.9% pure), N_2 and H_2 (both 99.99% pure) as the reactive gases. The total pressure during deposition was maintained at 100 Pa. A radio frequency was 13.56 MHz and the power supplied was 150 W. During deposition, the substrate was heated by a heating resistor at 450°C. The deposition time was 2 hours.

XRD pattern of the thin film was measured using diffractometer (Rigaku/TFD system) for thin film analysis under the condition of 50 V × 200 mA.

XPS spectra were measured using ESCA Lab-5 system (VG Scientific Co.) under a vacuum of 1×10^{-7} Pa or higher. Charging effect was corrected using C_{1s} peak (284.6 eV) as a standard one. Ar^+ ion sputtering was used for depth analysis. Sputter rate was about 10 Å/min. Impure elements were detected by SIMS using Ar^+ ion beam. A Hitachi IMA-SS spectrometer was used and operated at 10 KV below a vacuum conditions of 1×10^{-4} Pa.

The colour of titanium compound film deposited exhibited metallic dark blue. It is observed by SEM that the surface of the film is very smooth. The X-ray diffraction patterns are shown in **Fig. 1**. It can be considered that the film was identified as the mixture of TiO_2 and TiO phases. Further, it is observed that peak intensity due to (110) plane of α-phase increases after deposition. The increase of (110) peak may be attributed to chromium enrichment near the surface or prefered orientation of (110) plane.

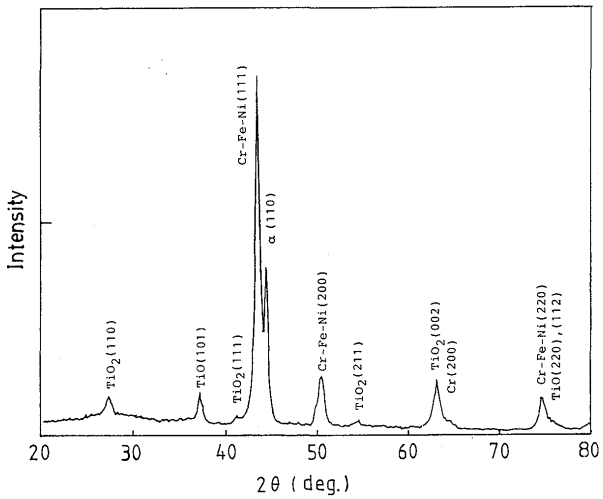

Fig. 1 X-ray diffraction patterns of the titanium compound film deposited by R. F. plasma-CVD on the SUS 316 stainless steel.

Nitrides was not detected with X-ray diffraction analysis but nitrogen was detected from SIMS analysis. In addition, it is found that impure elements are aluminum, silicon, chromium and iron. Futher, sodium, magnesium, manganese, phosphorus and sulfur were detected as trace elements.

Fig. 2 shows N_{1s}, Ti_{2p} and O_{1s} binding energies on deposited film measured with X-ray photoelectron spectra, respectively. As shown in Fig. 2 (a), the N_{1s} binding energy of 396.1 eV approximately corresponds with the result of titanium nitride (396 eV) given by E. Bruninx et al. [4]. Consequently, it is indicated that nitrogen exists in the form of titanium nitride or oxynitride.

The values of $Ti_{2p(1/2)}$ and the $Ti_{2p(3/2)}$ binding energies are respectively 464.1 and 458.4 eV. (see Fig. 2 (b)) These are close to Ti_{2p} peak positions on TiO_2. (464.2, 458.5 eV) The O_{1s} binding energy of 530.0 eV (see Fig. 2(c)) is also consistent with those of the oxides of group IV elements. (about 530.5 eV [4])

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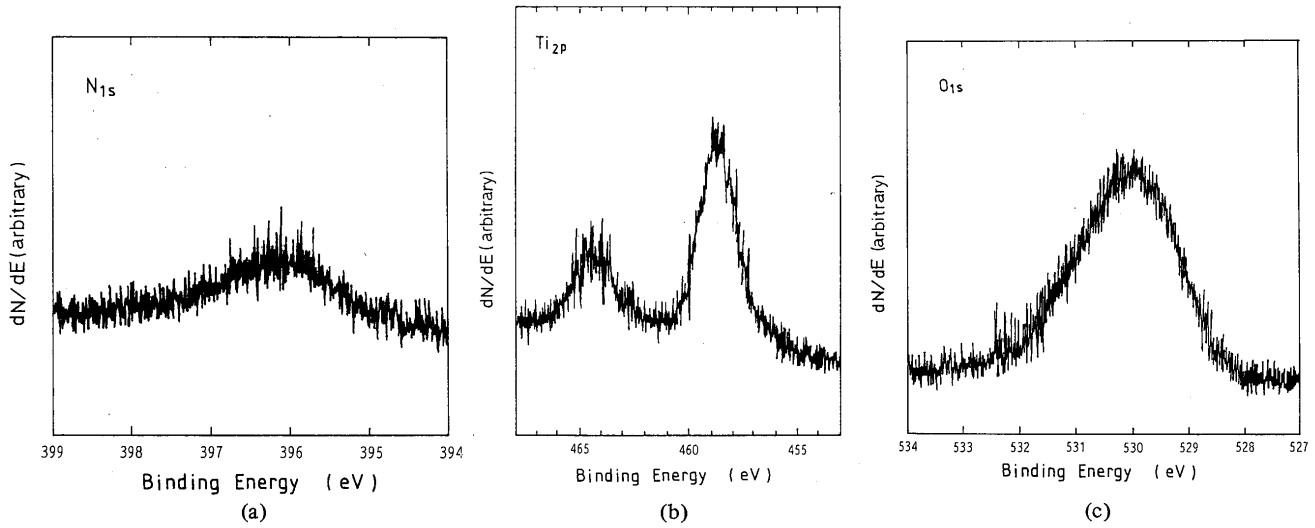

Fig. 2 X-ray photoelectron spectra of the titanium compound film after sputtering by Ar^+ ion beam in 5 minutes. (a) N_{1s}, (b) Ti_{2p} and (c) O_{1s} binding energies are shown respectively.

It is indicated that the deposited film consists of TiO_2 and TiO and titanium nitride phases. Further, TiO and TiN phases may form a oxynitride phase. Characterization of titanium compounds, particularly on the state of nitrides, oxides and oxynitrides, should be cleared in connection with the mechanical properties.

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