Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp557-558

Hydrophilic property of titanium oxide film crystallization induced by an oxidation nickel seed layer

Tan-Wei Lin[1], Bo-Sheng Chiang[1], Springfield Chang[2], Day-Shan Liu[1,*]

[1]Institute of Electro-Optical and Material Science, National Formosa University, Huwei, Yunlin 63201, Taiwan
[*]Tel: 886-5-6315665; Fax: 886-5-6329257; E-mail: dsliu@sunws.nfu.edu.tw
[2]Department of Optoelectronic Engineering, Far East University, Hsin-Shih, Tainan 74449, Taiwan

1. Introduction

Titanium oxide (TiO_2) films have applications as function coatings for excellent photocatalytic property and high refractive index [1-2]. The best photocatalytic activity is exhibited only by the TiO_2 film with anatase structure [3]. Though plasma-enhanced chemical vapor deposition (PECVD) is a common technique to prepare a high coverage and uniformity TiO_2 film, the deposited film possesses an amorphous structure [4]. An adequate post-annealing treatment is essential to activate film crystallization. In addition, the oxygen vacancy concentration in TiO_2 lattice accelerates the meta-stable anatase phase transformation even at low temperature, leading to an overall degradation in physical properties [5]. Accordingly, method to extend the appearance of anatase phase is crucial. A number of studies aimed to modify TiO_2 film performance were carried out by using metals or related oxides [6-7]. In this study, an oxidation nickel seed layer was used to induce and enhance the crystallization of the TiO_2 film. The effects on the thermo-induced and photo-induced hydrophilicity compared to a pure TiO_2 film were investigated and discussed from the XRD and surface morphology measurements.

2. Experimental procedure

A 20-nm-thick nickel layer was deposited on the silicon substrates and oxidized at 550°C for 1 min under oxygen ambient. Titanium oxide (TiO_2) film with a thickness of 250 nm prepared by PECVD using titanium tetraisopropoxide [$Ti(OC_3H_7)_4$, TTIP] and oxygen reactant gas was deposited onto the oxidation nickel seed layer at a temperature of 200°C. The configuration of the TTIP-PECVD system is shown in Fig. 1. A pure TiO_2 film was also prepared for comparison. These samples with and without a nickel oxide seed layer were annealed at temperatures of 300°C-600°C under oxygen ambient for 30 min. The crystalline structure and chemical bond natural were investigated using X-ray diffractometer (XRD) and Fourier transform infrared spectroscopy (FTIR) measurements. The surface morphologies were observed by scanning electron microscopy (SEM) with the accessory of the energy dispersive X-ray spectroscopy (EDS). The photocatalytic effect was evaluated from the surface hydrophilicity by measuring the water contact angle evolutions.

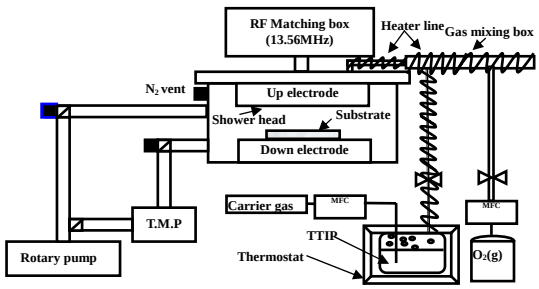

Fig.1 Configuration of the TTIP-PECVD system.

3. Experimental results

Figure 2 indicates the thermo-induced hydrophilicity as a function of storage time in darkness ambient for the annealed samples with and without the nickel oxide seed layer. The as-annealed samples exhibited super-hydrophilic surface and gradually degraded after storage for 3 hours. The thermo-induced hydrophilicity was ascribed to the reduction of the oxygen vacancies and the conversion of Ti^{3+} to Ti^{4+} in the TiO_2 film [8]. The presence of the nickel oxide seed layer was responsible for enhancing the above-mentioned mechanisms. The FTIR spectra of the as-prepared and annealed TiO_2/NiO_x structures are shown in the inset figure of Fig. 2. The peaks at 420 cm^{-1} and 3400 cm^{-1} were identified as the Ti-O vibration mode and terminal type of OH groups, respectively [2]. After thermal annealing, the spectra were dominated by Ti-O chemical bond. The higher the annealed temperature, the sharper and more intense is the Ti-O peak.

Figure 3 shows the water contact angle as a function of UV light irradiation time for the TiO_2 films with and without a nickel oxide layer annealed at 350°C. The photo-induced hydrophilicity of the annealed TiO_2 film with a seed layer was superior to that of the pure TiO_2 film. The inset XRD patterns in Fig. 3 indicate the difference in the crystalline structures. The annealed TiO_2/NiO_x film showed obviously TiO_2 anatase phase, while no diffraction peak was observed from the annealed TiO_2 film, revealing that the nickel oxide

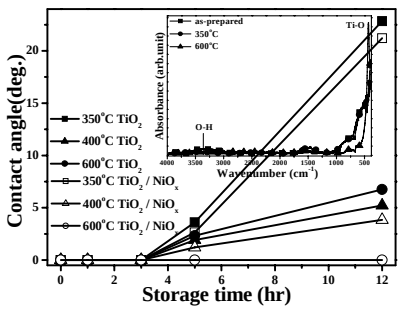

Fig.2 Water contact angle as a function of storage time for the annealed samples with and without a nickel oxide seed layer. The inset figure indicates the FTIR spectra of the as-prepared and annealed TiO_2/NiO_x samples.

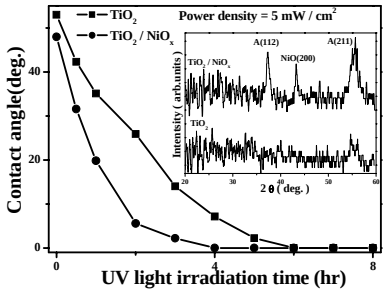

Fig.3 Water contact angle as a function of UV light irradiation time for the TiO_2 films with and without a nickel oxide layer annealed at 350°C. The associated XRD spectra are shown in the inset figure.

seed layer was able to lower the crystallized temperature of TiO_2 film. The X-ray diffraction patterns of the TiO_2 film with and without a nickel oxide seed layer annealed at 400 and 600°C is shown in Fig. 4. All the diffraction patterns showed obviously anatase crystalline structure with dominated phase of A(101). The FWHM of the A(101) phase for the annealed TiO_2/NiO_x films was narrower than that of the annealed TiO_2 films, indicating that the anatase structure in the annealed TiO_2 film was facilitated by the nickel oxide seed layer. In addition, the evolution of FWHM in the TiO_2/NiO_x films annealed from 400°C to 600°C (0.62° to 0.52°) was opposite to that of the annealed TiO_2 films (0.66 to 0.72°). The wider FWHM of the A(101) phase observed from the pure TiO_2 film annealed at high temperatures was attributed to the mechanism of anatase-rutile phase transformation [10]. As a result, the phase transformation of the TiO_2 film annealed at high temperatures was suppressed by using the nickel oxide seed layer. The associated photo-induced hydrophilicity as a function of the UV light irradiation time (1 mW/cm^2) is illustrated in the inset figure of Fig. 4. The annealed samples achieved super-hydrophilic surface after irradiation time reaching 30 min. The best anatase crystalline structure obtained from TiO_2/NiO_x film annealed at 600°C resulted in the excellent surface hydrophilicity as a consequence of the superior photocatalytic effect. The surface morphology of the as-prepared TiO_2/NiO_x structure is shown in Fig. 5(a). The surface had ambiguous contour with round distributed grains. The surface morphology and the EDS spectra of the crystallization TiO_2 films with and without a nickel oxide seed layer annealed at 600°C are given in Figs. 5(b) and (c), respectively. The particles in Fig. 5(b) was randomly

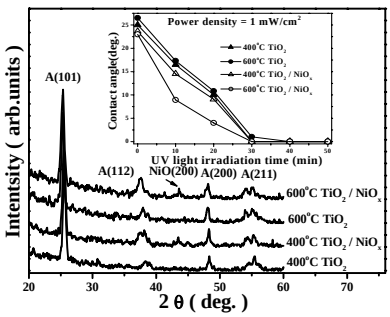

Fig.4 X-ray diffraction patterns of the TiO_2 film with and without a nickel oxide seed layer annealed at 400 and 600°C. The associated photo-induced hydrophilicity as a function of the UV light irradiation time is illustrated in the inset figure.

distributed, while that in Fig. 5(c) was more uniform and was separated into several clusters. The cluster distribution was influenced by the island-like distributions of the nickel oxide seed layer shown in Fig. 5(d). The crystal growth dimension was suggested to be constrained due to the cluster structures and thus enhance and extend the anatase crystallization after thermal annealing.

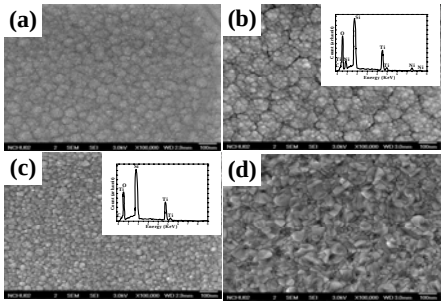

Fig.5 Surface morphology of (a) as-prepared TiO_2/NiO_x film, (b) TiO_2/NiO_x film annealed at 600°C, (c) pure TiO_2 film annealed at 600°C and (c) (d) nickel oxide seed layer. EDS spectra are shown in the inset figures.

4. Conclusions

An oxidation nickel seed layer was employed to induce the crystallization of TiO_2 film. From the thermo-induced hydrophilicity study, the nickel oxide seed layer had the ability to compensate the oxygen vacancies and enhance the Ti^{4+} activation in the TiO_2 film after thermal annealing, resulting in a longer storage time in darkness ambient. The associated XRD diffraction patterns of the annealed samples also indicated that this seed layer was able to induce and facilitate the crystallization of TiO_2 anatase phase, performing a superior photo-induce hydrophilic property. In addition, the anatase-rutile phase transformation of the TiO_2 film annealed at 600°C was suppressed due to the specific cluster structures that were correlated with the island-like oxidation nickel seed layer.

Acknowledgments

This work was supported by the National Science Council of the Republic of China under NSC96-2221-E-150-072-MY3.

References

[1] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, Jr., Science **297** (2002) 2243.
[2] D. S. Liu, T. W. Lin, B. W. Huang, F. S. Juang, P. H. Lei, and C. Z. Hu, Appl. Phys. Lett. **94** (2009) 143502.
[3] T. Sekiya, S. Ohta, M. Hanakawa, and S. Kurita, J. Phys. Chem. Solids **62** (2001) 717.
[4] M. Nakamura, S. Kato, T. Aoki, L. Sirghi, and Y. Hatanaka, J. Appl. Phys. **90** (2001) 3391.
[5] S. Riyas, V. A. Yasir, and P. N. M. Das, Bull. Mater. Sci. **25** (2002) 267.
[6] B. F. Xin, Z. Y. Ren, P. Wang, J. Liu, L. Q. Jing, and H. G. Fu, Appl. Surf. Sci. **253** (2007) 4390.
[7] H. H. Huang, H. P. Chang, F. H. Wang, Y. S. Liu, M. C. Wang, and D. F. Lii, Jpn. J. Appl. Phys. 47 (2008) 764.
[8] Q. Ye, P. Y. Liu, Z. F. Tang, and L. Zhai, Vacuum **81** (2007) 627.
[9] Xin Zhang, Qingquan Liu, Appl. Surf. Sci. **254** (2008) 4780.