Ceramics International 22 (1996) 95–99
© 1996 Elsevier Science Limited and Techna S.r.l.
Printed in Great Britain. All rights reserved
0272-8842/96/$15.00

0272-8842(95)00062-3

Optical and Microstructural Properties of $TiO_2(Ni^{2+})$ Thin Films

C. Parlog, M. Gartner, P. Osiceanu, V. Teodorescu,[a] F. Moise[b] & A. Ianculescu

Institute of Physical Chemistry, Spl. Independentei 202, 77208 Bucharest, Romania
[a]Institute of Physics and Technology of Materials, Bucharest-Magurele, PO Box MG-7, Bucharest 76900, Romania
[b]ZECASIN - SA, Spl. Independentei 202, 77208 Bucharest, Romania

(Received 12 November 1994; accepted 1 March 1995)

Abstract: Coloured $TiO_2(Ni^{2+})$ thin coatings doped with transitional metals (Ni) were deposited on different substrates (silicon wafers, glass, aluminum) by the sol–gel dip coating process. Complementary techniques (XPS, SE, TEM, XRD, Absorption Spectroscopy) were used to characterize the surface stoichiometry and optical properties, as well as the structure and texture of the thermally treated gels. The presence of fully oxidized film in the outer layers, crystallization in heat treatment to anatase and rutile, formation of porous and coloured films due to the influence of the dopant and the reaction with the substrate, as well as a decrease by three orders of magnitude of the resistivity of Ni-doped films, are reported.

1 INTRODUCTION

TiO_2 films have many interesting (physical, structural, optical) properties, which make them suitable for applications in antireflective coatings,[1,2] in microelectronics devices[3,4] (due to their high dielectric constant), etc. The doping of these films enlarges the field of applications to colour filters[5] and electrochromism materials for display devices.[6]

The sol–gel method is a suitable deposition technique for TiO_2 films. It offers a great possibility of adjusting the film properties by changing the composition of the solution, doping, etc.

In this paper we analyze the influence of the substrate, dopant and thermal treatment temperature upon the surface chemical composition, microstructure and optical properties of the $TiO_2(Ni^{2+})$ films.

2 EXPERIMENTAL

2.1 Preparation of the nickel-doped TiO_2 films

The oxidic films were deposited on three different substrates (soda-lime glass, single-crystal silicon wafers and aluminum film/soda lime glass). These substrates were dip-coated from titanium isopropyl solution in ethanol. Nickel was introduced in a molar ratio: $NiCl_2{\cdot}6H_2O$: $Ti(iOC_3H_7)_4$ = 0·025. The sol was stabilized with CH_3COOH. After aging the sol for three days, homogeneous coatings were obtained from sol with viscosity 3·1 cps. The films were dried in air at room temperature for 24 h and then heated in air for 1 h at each of the following temperatures: 300, 500, 700 and 800°C.

The solution composition and experimental conditions were presented in previous papers.[5,7]

2.2 Film characterization

The values of density (Table 1) were determined using the flotation method in a $ZnBr_2$ aqueous solution.[8]

In order to check the film stoichiometry and the cleanliness of the surface (mostly covered with carbon contaminant) an XPS study was performed using an ESCALAB Mk II equipment.[7]

Phase identification of the thin layer was made using an X-ray diffractometer.[5]

The structure and the morphology of the thin films were examined by transmission electron microscopy (TEM) and selected area electron

Table 1. Density (ρ), refractive index (n) and thickness (d) of $TiO_2(Ni^{2+})$ films as a function of the substrate (Al, Si, glass) and temperature of thermal treatment (T)

	ρ(g/cm³)			n			d(Å)		
T(°C) / Substrate	300	500	700	300	500	700	300	500	700
Al	1·81	—	—	2·693	—	—	308	—	—
Si	1·80	1·84	1·89	2·276	2·322	2·474	466	303	280
Glass	1.74	1·79	—	1·870	1·880	—	534	500	—

diffraction (SAED) using an extraction replica method in a JEOL 200 CX electron microscope.

The refractive index and coating thickness (Table 1) were obtained by multiangle spectroellipsometric (SE) technique over the spectral range 300–700 nm.[7]

The presence of Ni as dopant in the TiO_2 matrix can be traced by its absorption band in the 700–750 nm range (inaccesible to ellipsometric spectroscopy) using reflectance spectroscopy.[5]

The resistivity of films was obtained from I–V measurements.

3 RESULTS AND DISCUSSION

3.1 Surface chemical composition of TiO_2/Si

The 2p XPS spectrum of titanium exhibits the well-known binding energies and the shape characteristics of TiO_2 (458·8 eV for 2p3/2 line and 464·5 eV for 2pl/2 line). This conclusion is also supported by quantitative XPS analysis. To perform this analysis we used the sensitivity Scofield factors corrected for two monolayers of adsorbed contaminant, escape depth and transmission function, taking into account their energy dependence for 1s oxygen and 2p titanium binding energies. Other corrections have been carried out for the oxygen bound to carbon (Fig. 1) and found in hydroxyl groups bound to titanium in the first atomic layers (Fig. 2).

On the expanded spectra of these elements detailed investigation has been carried out by the deconvolution procedure. The data processing included a background subtraction by Shirley method and a curve fitting with two peaks using four parameters: peak position, full width at half maximum (FWHM), Gaussian–Lorentzian mixture ratio and intensity 2p3/2:2pl/2 lines constraint ratio.

The results of this analysis are the following: the C 1s main peak is found to have the binding energy at 284·6 eV assigned to graphitic carbon and a broader and low intensity peak situated at 286·7 eV assigned to C–O bonding. The O 1s low bonding energy peak (529·8 eV) corresponds to TiO_2, while the higher binding energy peak (531·9 eV) could be assigned to hydroxyl groups[9,10] bound on the sample surface. Accounting for all these correction factors, the concentration ratio (intensity O 1s/intensity Ti 2p) can be evaluated at 1·95 (± 0·5) proving the stoichiometry of fully oxidized titanium film.

3.2 The microstructure of TiO_2 films

The influence of the substrate nature (Al, Si, glass), the temperature of thermal treatment (300–800°C) and the dopant (Ni^{2+}) upon the crystalline phase of TiO_2 films was evidenced by X-ray diffraction (XRD), spectroellipsometry (SE) and TEM.

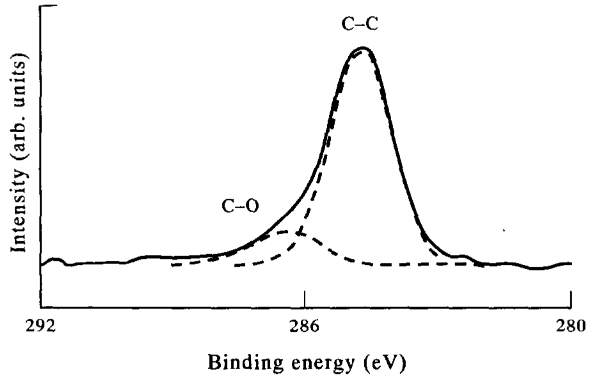

Fig. 1. XPS spectrum of carbon 1s line.

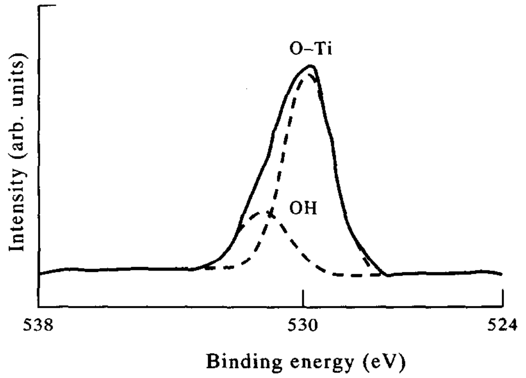

Fig. 2. XPS spectrum of oxygen 1s line.

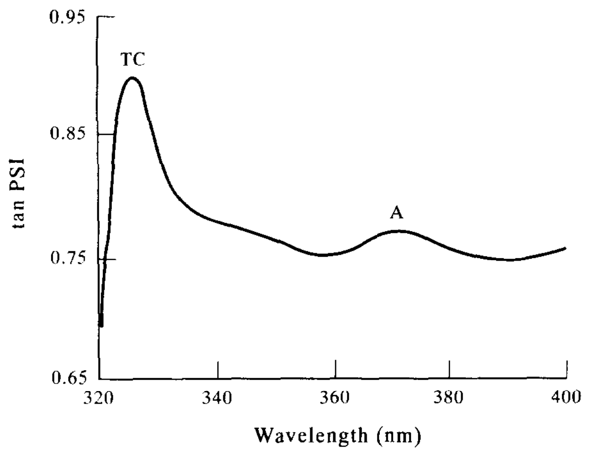

Fig. 3. Ellipsometric spectrum of $TiO_2(Ni^{2+})$/Al thermally treated for 1 h at 300°C. (A – anatase; TC – charge transfer absorption band); tan PSI = ellipsometric parameter.

3.2.1 Substrate

As shown by the ellipsometric spectra[7] in TiO_2/Si films an incipient crystallization took place at 300°C while the TiO_2/glass films were completely amorphous. The reasons for this behaviour are the following: the substrate topography[1] (on a crystalline substrate the film itself is more liable to crystallize) and the diffusion of various species[1,10] (mainly Na which acts as dopant — see section 3·2·3) from glass into the film which favours its amorphous character. Even a TiO_2-doped film can crystallize at 300°C if the substrate is crystalline, as shown by the ellipsometric spectrum of $TiO_2(Ni^{2+})$/Al (Fig. 3), as well as by the TEM picture (Fig. 4a).

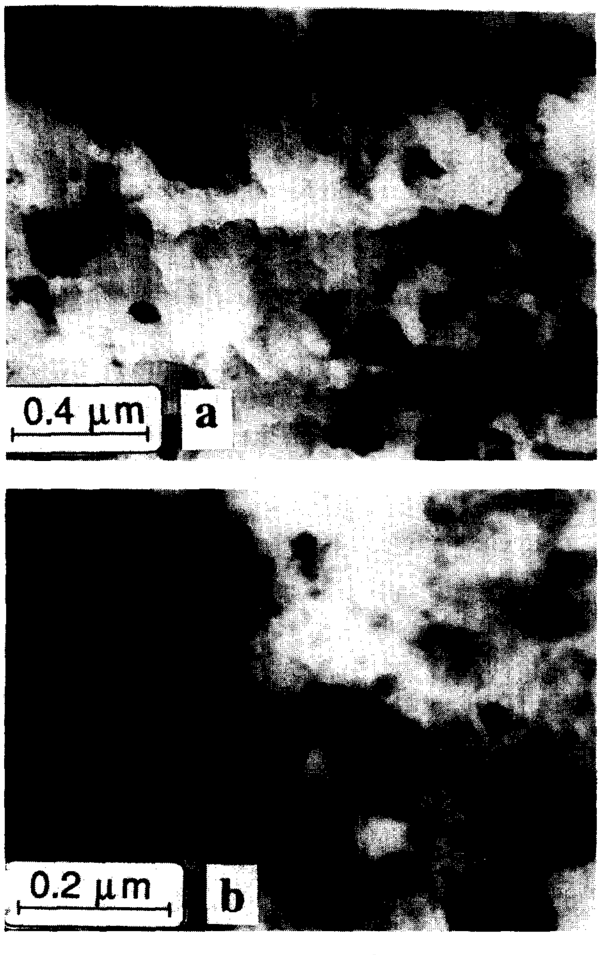

Fig. 4. TEM images of the $TiO_2(Ni^{2+})$/Al thin film after a thermal treatment at: (a) 300°C; (b) 500°C.

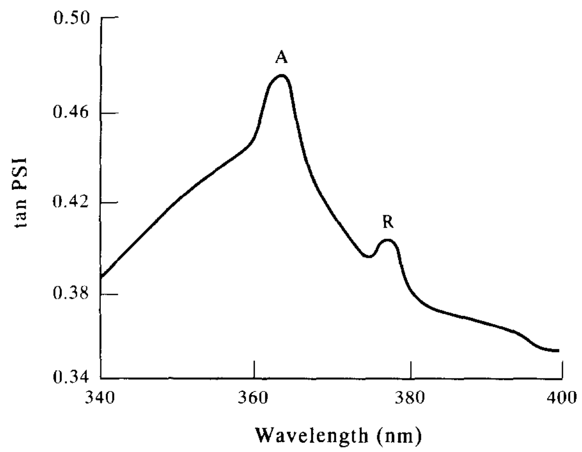

Fig. 5. SE spectrum of TiO_2/Si thermally treated for 1 h at 700°C (A – anatase; R – rutile).

3.2.2 Thermal treatment

A discussion about the influence of the thermal treatment of TiO_2 films can be made only depending on the substrate. On the Al substrate the 500°C thermal treatment of the $TiO_2(Ni^{2+})$ films led to a strong change of the thin films. This is due to the chemical reaction between the Al and TiO_2, with the formation of a complicated structure of $TiO_x+Al_2O_3$ thin films appearing in black colour as shown in Fig. 4b.

For the glass substrate a temperature higher than 500°C led to its melting.

Only for the Si substrate is it possible to make a thermal treatment up to 800°C. For the TiO_2/Si film SE showed the appearance of rutile (R) phase even at 700°C (Fig. 5) and for $TiO_2(Ni^{2+})$/Si, X-ray diffractograms identify rutile at 800°C (Fig. 6).

3.2.3 Dopant

The introduction of dopants (Ni^{2+}) in TiO_2/Si films inhibits their crystallization, the crystalline phases appearing at higher temperatures: the anatase (A) was evidenced by SE only at 500°C (and only from 700°C by XRD — Fig. 6) and the rutile started at 800°C.[11] It is obvious that one may obtain the desired crystalline phase by adjusting these three factors (substrate nature, thermal treatment and dopant).

3.3 Optical properties

The optical properties are strongly influenced by the same factors, in a way that is detailed as follows:

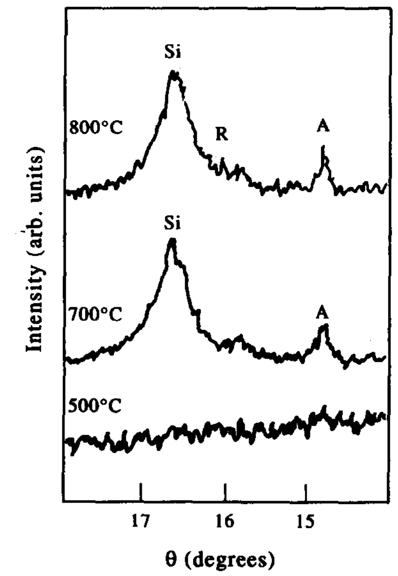

Fig. 6. X-ray diffractogram of TiO$_2$(Ni^{2+})/Si (A-anatase; R – rutile; Si-substrate).

(a) SE spectra of TiO$_2$(Ni^{2+}) deposited on Al, Si and glass substrates (Fig. 7) and thermally treated at 300°C showed a shift of charge transfer adsorption band (TC) from 350 nm (glass) to 330 nm (Si) and 320 nm (Al). This shift is correlated with the lowering of the film thickness and the increase in the refractive index (see Table 1). These results are in good agreement with the changes in density values (see also Table 1) when different substrates are used.

(b) After a thermal treatment up to 800°C, TiO$_2$(Ni^{2+})/Si films became thinner and denser (see Table 1). The lowering of the film thickness is also evidenced by the shift of electronic band of TiO$_2$ to UV with increasing temperature.[2]

(c) The dopant introduced in the oxidic matrix has as main effect the colouring of the film. Ni introduces a band in 700–750 nm range which is not shown by SE, but is well established by absorption spectroscopy. In Fig. 8 is shown up a band with the peak at 715 nm, attributed to $^{3}T_{1}g$–$^{3}A_{2}g$ transition, specific for the octahedral Ni^{2} (3d^{8}) complexes.[12]

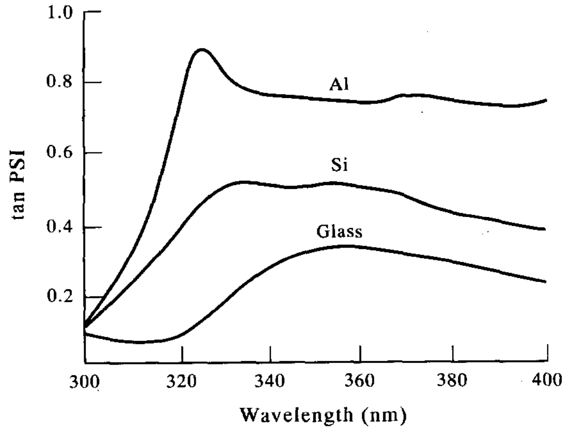

Fig. 7. SE of TiO$_2$(Ni^{2+}) thermally treated 1 h at 300°C depending on the substrate.

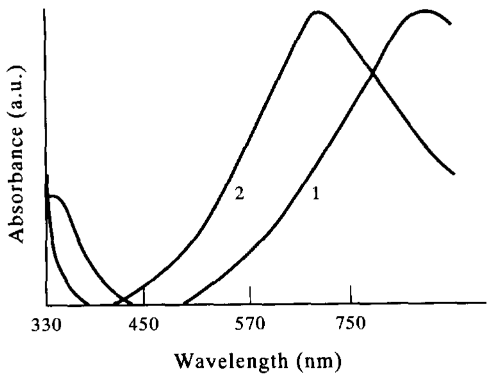

Fig. 8. Absorption spectra of TiO$_2$(Ni^{2+})/Si: 1 – untreated film; 2 – treated film at 300°C.

Another effect of introducing dopants is that the films become more porous and the refractive index becomes lower (see Table 1).

The resistivity of the TiO$_2$/Si film (heated at 500°C) is $10^{10}\Omega$ cm for TiO$_2$(Ni^{2+})/Si. A similar decrease by three orders of magnitude was obtained by Xu *et al.* after heating TiO$_2$ films in H$_2$ at 500°C.

4 CONCLUSIONS

1. The tendency of TiO$_2$ films to crystallize to anatase and rutile forms without degradation of the film quality has been demonstrated.
2. The introduction of dopants inhibited this crystallization, increased the porosity of the films and coloured them.
3. The resistivity of TiO$_2$(Ni^{2+})/Si films thermally treated for 1 h at 500°C was three orders of magnitude lower than the resistivity of TiO$_2$/Si.
4. The TiO$_2$/Si samples showed the right stoichiometry of a fully oxidized film in the first atomic layers.

REFERENCES

1. YOLDAS, B., *Appl. Opt.*, **21** (1982) 2960.
2. PETTIT, B., BRINKER, C. J. & ASHLEY, C. S., *Solar Cells*, **15** (1985) 267.
3. PAPINI, M., *J. Appl. Phys.*, **70** (1991) 777.
4. VOPOTILOV, K. A., ORLOVA, E. V. & PETROVSKY, V. I., *Thin Solid Films*, **207** (1992) 180.
5. ZAHARESCU, M., PARLOG, C., CRISAN. M., GARTNER, M. & VASILESCU, A., *J. Non-Crystalline Solids*, **160** (1993) 162.
6. OZER, N., TEPEHAN, F. & BOZKURT, N., *Thin Solid Films*, **219** (1992) 193.
7. GARTNER, M., PARLOG, C. & OSICEANU, P., *Thin Solid Films*, **234** (1993) 561.

8. SMITH, F. W., *J. Appl. Phys.*, **55** (1984) 764.
9. TURKOVIC, A., SOKCEVIC, D., VALLA, T., MILUN, M. & RUKAVINA, J., *Fizika*, **A2** (1993) 23.
10. TRAPALIS, CH., KOZHUKHAROV, V., SAMUNEVA, B. & STEFANOV, P., *J. Mater. Sci.*, **28** (1993) 1276.
11. SAMUNEVA, B., KOZHUKHAROV, V., TRAPALIS, CH. & KRANOLD, R., *J. Mater. Sci.*, **28** (1993) 2353.
12. LEVER, A. B. P., *Inorganic Electronic Spectroscopy*. Elsevier, Amsterdam, 1968.
13. XU, W. W., KERSHAW, R. DWIGHT, K. & WOLD, A., *Mater. Res. Bull.*, **25** (1990) 1385.