Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solar Energy Materials & Solar Cells
ELSEVIER
Solar Energy Materials & Solar Cells 86 (2005) 299–308
www.elsevier.com/locate/solmat

Characterization of TiO_2 deposited on textured silicon wafers by atmospheric pressure chemical vapour deposition

B. Vallejo[a,*], M. Gonzalez-Mañas[a], J. Martínez-López[a], F. Morales[b], M.A. Caballero[a]

[a]*Departamento de Cristalografía, Faculdad de Ciencias, Universidad de Cádiz, 11500 Puerto Real, Spain*
[b]*Departamento de Ciencia, de los Materiales e Ingeniería Metalúrgica, Faculdad de Ciencias, Universidad de Cádiz,11500 Puerto Real, Spain*

Received 25 March 2004; accepted 29 July 2004
Available online 12 October 2004

Abstract

Thin films of TiO_2 have been deposited on textured silicon wafers. The technique used has been atmospheric pressure chemical vapour deposition (APCVD). This technique is interesting for its high production rate and low cost. The film structure has been studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that the "as-deposited" film is amorphous and inhomogeneous, and it presents a double layer. We suggest that the inner one is constituted by silicate and the outer layer corresponds to the TiO_2 film. After heat treatment, the outer layer undergoes a phase transition from amorphous phase to crystalline. The TEM images show small anatase crystals.

Keywords: Titanium dioxide; Atmospheric pressure chemical vapour deposition (APCVD); Texturization; Antireflective coatings

*Corresponding author.
E-mail address: beatriz.vallejo@uca.es (B. Vallejo).

0927-0248/$ - see front matter
doi:10.1016/j.solmat.2004.07.011

1. Introduction

Titanium dioxide (TiO_2) is a large band gap semiconductor with many interesting properties. It is transparent to visible light, has a high refractive index and low absorption and consequently, it is widely used as an optical coating material [1,2]. Particularly, it is well known that the application of a coating layer on the front surface of the photovoltaic cells reduces the amount of reflection of the incident light, which improves the device performance.

Thin films of TiO_2 are deposited on silicon substrates by a number of methods, such as e-beam evaporation [3], sputtering [4], sol–gel process [5] and chemical vapour deposition [6]. Each method has its own advantages and disadvantages. In some cases, the process is extremely time consuming and makes the deposition apparatus complicated and expensive.

The films can be processed at a relatively low cost with high throughput using atmospheric pressure chemical vapour deposition (APCVD) [7]. Several studies on TiO_2 formed by this technique have been reported. Wong et al. [7] studied the properties of TiO_2 deposited on polished silicon wafers. They investigated different annealing temperatures. Their results suggest that the film after the heat treatment has gone through a phase transition from amorphous-like to crystalline. Lemiti et al. [8] deposited TiO_2 films on heated silicon substrates. Afterwards, they used rapid thermal annealing in the 400–700 °C range to adjust simultaneously the refractive index and the thickness of titanium oxide layers in order to achieve an antireflection coating in industrial conditions.

It is known that the preparation conditions of TiO_2 thin films can strongly affect the physical properties of the film. Control of refractive index and thickness of the thin films is very important to produce suitable material for optical applications. Therefore, it is necessary to study systematically the structural and optical properties of TiO_2 thin films according to preparation conditions.

In this paper, TiO_2 thin films have been prepared by APCVD technique using textured silicon wafers as substrate. It should be noted that the majority of the published works utilize polished silicon, float glass and SiO_2 as substrate, since the utilization of texture surface like substrate makes the homogeneous deposition of layers on it difficult. We have focussed our attention on the morphology and crystalline structure of TiO_2.

2. Experimental

TiO_2 thin films were deposited by APCVD at 400 °C. In the case of APCVD, two methods can be used from organometallic vapour. In this case, we have used the hydrolysis of the isopropoxide Ti $(OC_3H_7)_4$ (TPT).

Subsequently, the coated samples were heated up to 810 °C in order to remove solvent, residual organic and increase the film density.

The structure characterization of thin films has been performed using X-ray diffraction (Philips PW 1710) with CuK_α radiation. The angular domain was

between 5 and 60°. Since the diffraction peaks of silicon are very strong, no diffraction peaks of titanium oxide can be identified on XRD patterns when a layer of TiO_2 is deposited; then for this characterization several films were deposited on the silicon substrate.

For the TEM investigation, cross-sectional specimens were prepared. Two small chips were glued together face to face and held by a copper ring. The samples were thinned by mechanical polishing and then argon milling on both sides at a small incident angle. The microstructural observations were performed using a Jeol JEM-1200EX/(DCS) transmission electron microscopy operating at 120 KV.

Spectroscopy ellipsometry (SE) is known to be a powerful non-destructive technique to investigate the optical properties of films. Ellipsometric measurements have allowed us to determinate the refractive index and the thickness of the film. They were carried out at room temperature with a single wavelength ($\lambda = 632$ nm) at the incident angle of 70°. This technique needs a reflecting surface so we have deposited the film on a polished silicon substrate.

3. Results and discussion

In order to obtain films with good antireflective properties it is necessary to adjust the thickness and the refractive index. These parameters depend on the morphology and crystalline structure of TiO_2.

Titanium dioxide has three crystal structures: anatase, brookite, and rutile [9]. All three forms occur in nature, although rutile is the most common. The anatase is more stable than the rutile form for temperatures lower than 800 °C.

X-ray measurements have been performed in the "as-deposited" film and annealed films at 810 °C. In the first case, the diffractogram obtained shows only the diffraction peaks corresponding to silicon. It indicates that the TiO_2 film "as deposited" is amorphous. In the second one, the X-ray pattern obtained (Fig. 1) presents diffraction maximums corresponding to silicon in addition with other peaks that can be indexed as anatase lattice. These results are in accordance with the ones published by the other authors. Lemiti et al. [8] have shown that all films are amorphous as grown but annealing in air causes crystallization.

The TEM observations are in accordance with the X-ray results. Fig. 2 shows the TEM image of the TiO_2 film as deposited on textured wafer. An image taken with a major magnification as compared to the previous one (Fig. 3) allows us to see the following: first, that the film thickness is different in opposite faces of a same pyramid and second, that the TiO_2 film presents two layers clearly differentiated. This double layer is present in the TEM images of other authors that have used the same deposition method [7] but we have to remark that they do not make any mention of this fact.

The difference of thickness in the opposite face of a pyramid might be attributed to the method of deposition. The wafers are on a transporter tape that moves to a certain speed, the effect produced is equivalent to that which would occur if the speed of exit of the products across the reaction head had a horizontal component.

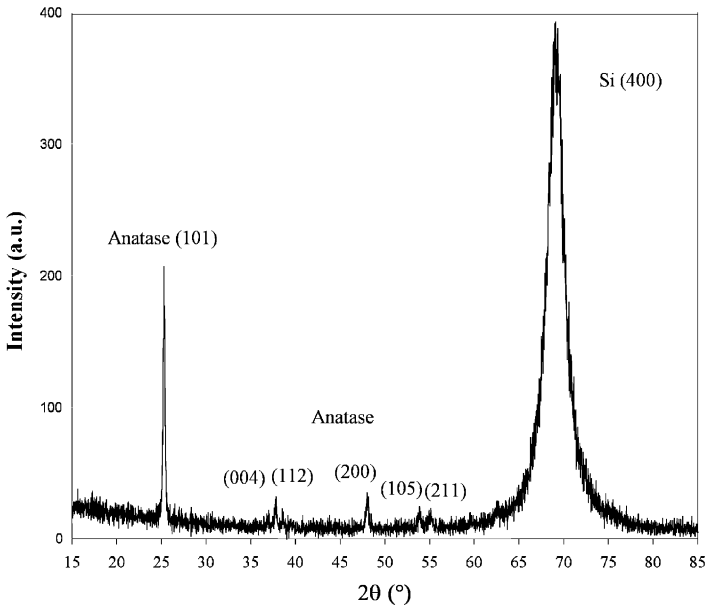

Fig. 1. X-ray diffraction patterns of TiO_2 thin films after heat treatment at 810 °C.

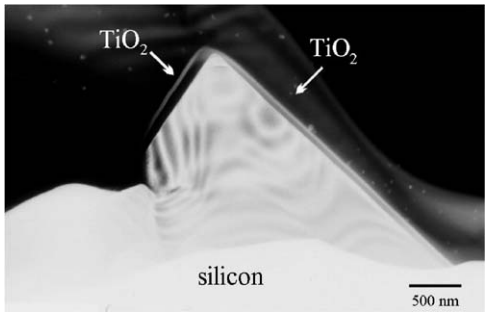

Fig. 2. TEM image of TiO_2 thin film deposited at 400 °C on textured silicon wafer.

To study the structure of the double layer we have performed electron diffraction. The diffraction patterns, shown in Fig. 4, confirm the X-ray results. The presence of the diffuse rings which are typical of the amorphous phase, indicates that the TiO_2 double layer does not present any crystalline structure. In Fig. 4 we can observe the presence of diffraction points. The points situated in the inner ring are due to the crystallization of the glue used for the sample preparation; the other ones correspond to diffraction pattern of silicon.

What happens when the double layer is annealed? Fig. 5 shows the TEM image of the TiO_2 film after annealing at 810 °C. In this figure, one can note that after heat

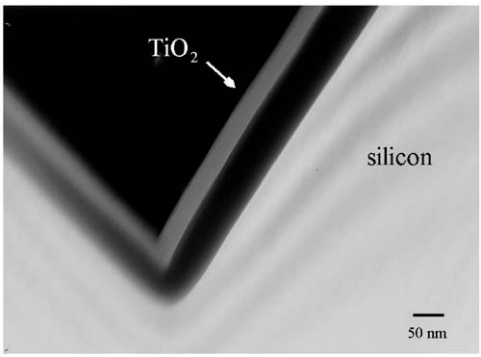

Fig. 3. TEM image of TiO_2 thin film deposited at 400 °C showing the double layer and the different thickness in opposite faces of the pyramid.

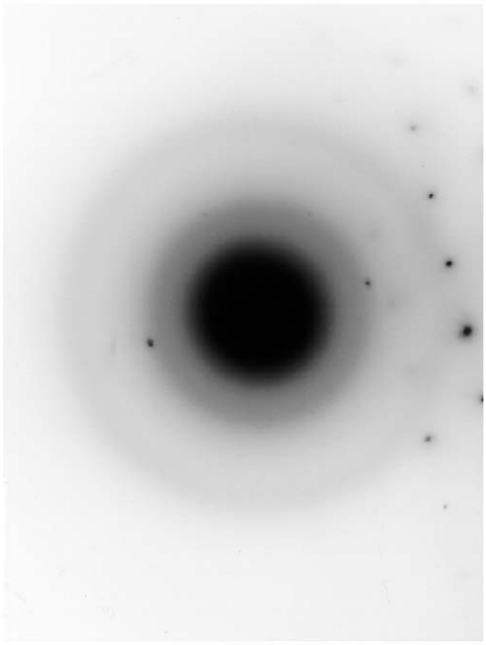

Fig. 4. Electron diffraction pattern of TiO_2 thin films deposited at 400 °C.

treatment the outer layer presents small crystals whereas the inner layer continues to be amorphous.

In order to identify the small crystals mentioned previously we have performed electron diffraction on these samples after annealing (Fig. 6). The pattern reveals the presence of three crystalline lattices superposed to the amorphous ring. The one most

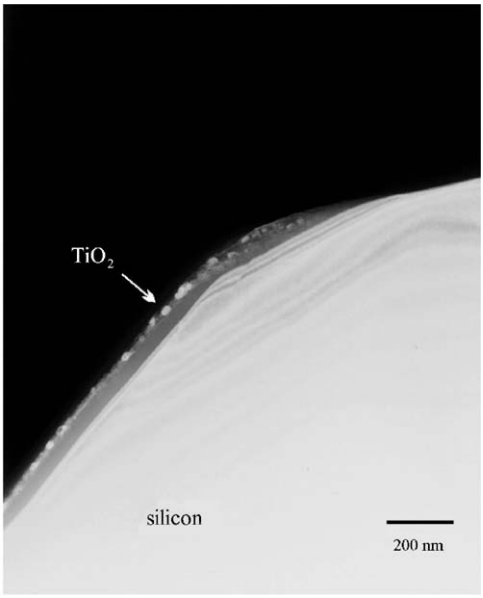

Fig. 5. TEM image of TiO_2 thin film after heat treatment at 810 °C showing small crystals on the surface.

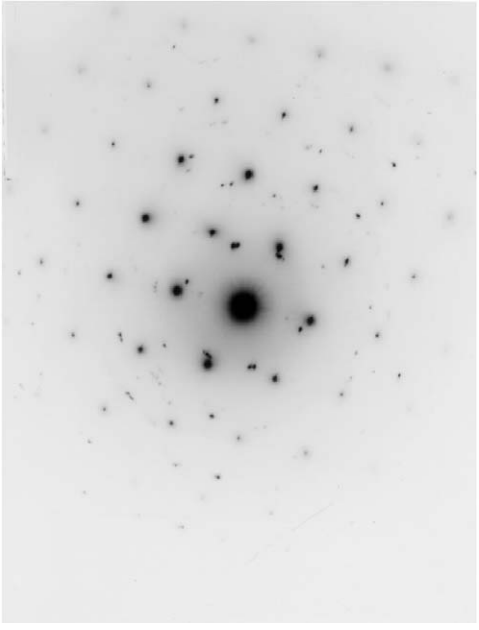

Fig. 6. Electron diffraction pattern of TiO_2 thin film after heat treatment at 810 °C detecting anatase phase.

intense corresponds to the silicon lattice. The two others correspond to the same crystalline lattice but are slightly disoriented. The analysis of these data has been performed with electron microscopic image simulation; the results show that the diffraction pattern is compatible with anatase diffraction according to the axis zone [–3–1–1]. Obviously, these results are in agreement with those obtained by X-ray diffraction.

Which is the origin of the double layer? We could think that it takes place as consequence of a gradient of temperature during the deposition. If this hypothesis was true, the annealing at 810 °C would result in unique layer constituted by TiO_2 nanocrystals in all its thickness; however, this fact has not been confirmed because the inner layer stays in the amorphous phase after annealing.

Another hypothesis would be that the origin of the double layer is due to the experimental set-up etc. used for the deposition. In order to investigate this, we have prepared silicon wafers with two TiO_2 films and others with only one film deposited on them. The aim of this is to study if the coated film, in the case of the two TiO_2 films, is still a double layer A, B or on the contrary it presents a multilayer structure A, B, A, B. We have denoted "layer A" as the inner one of the double layer observed in Figs. 3 and 5 and "layer B" as the outer one.

These samples have been studied "as deposited" and after annealing by TEM (Figs. 3, 5 and 7). In order to clarify the contrast observed we have schematically represented the results in Fig. 8.

In scheme 8(a), "as-deposited" sample, we can see that in both cases, when one film is deposited and when two films are deposited, the double layer has been formed and it is in amorphous phase. It should be pointed out that the thickness of the inner layer is the same in both cases.

In scheme 8(b), annealed sample, it can be seen that the double layer continues existing in both cases (one film and two films), but it is important to note that the inner layer is an amorphous phase and the outer one presents small crystals in all its

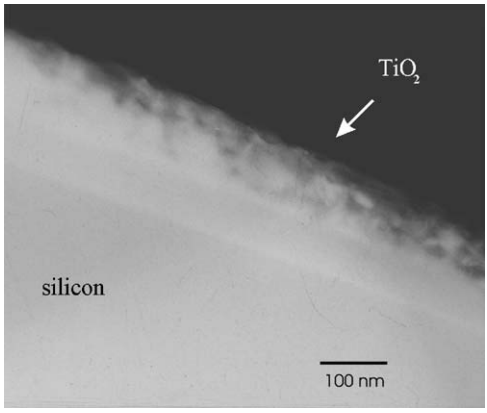

Fig. 7. TEM image of several films of TiO_2 after heat treatment at 810 °C showing small crystals on the surface.

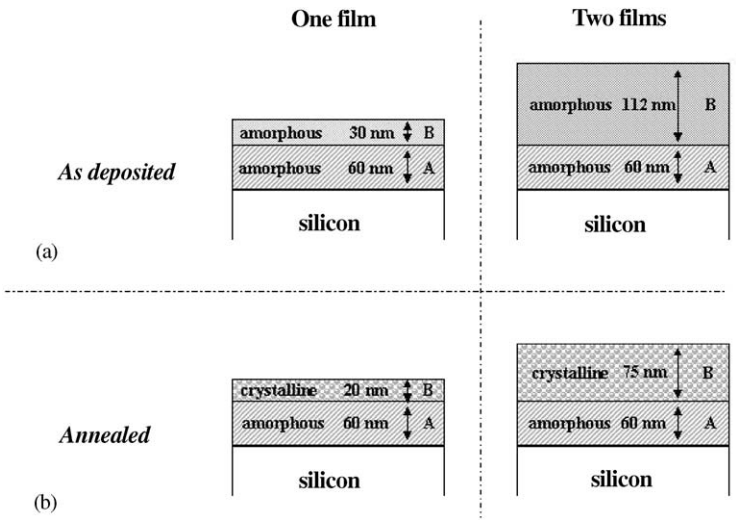

Fig. 8. Schematic representation of the double layer comparing one film and two films deposited in both cases: (a) "as-deposited" and (b) after annealing. (The measure error has been estimated to be about 10%.)

thickness. These crystals have been assigned by electron diffraction to anatase phase. It should also be pointed out that the thickness of the inner layer is the same in both the cases and its value coincides with the obtained one for the "as-deposited" sample.

These results make us think that the double layer is not due to the experimental set-up used for the deposition. We suggest that during the deposition of the TiO_2 film, the formation of an interface of amorphous material (A) takes place directly on the silicon substrate and the TiO_2 layer (B) is situated on the top of this interface.

The TEM images show that the transition from one to another is rather sharp. The formation of the TiO_2 layer occurs when the interface has reached a determined thickness. We have estimated its value to about 60 nm. After annealing at 810 °C, the TiO_2 layer (B) undergoes a phase transition of amorphous to crystalline (anatase phase); however, the interface (A) stays in the amorphous phase. This can be attributed to a different chemical composition between layers A and B. Other researches have reported the formation of a thin amorphous layer (20–40 Å) [10–12]. They deposit the film on Si (1 1 1) through chemical vapour deposition in ultra-high vacuum. Taylor et al. [10] have proposed that this layer consists of a mixture of Ti and Si oxides. Sandell et al. [11,12] observed that the composition of this layer changes with the thickness. In our case, we suggest that the interface (A) might be constituted by silicate of the type $TiSi_xO_y$. The assumption that the silicate is formed motivates an analysis of the chemical composition of the film. This is actually under study in our laboratory.

On the other hand, the validity of the APCVD as a deposition technique of antireflective coating requires that the thickness of the film deposited is uniform all over the wafer surface. The measurements of antireflective coating thickness by means of electron microscopy offers us a value in a wafer point, and due to this fact we have looked for other techniques that allow us to study the uniformity of the thin film thickness deposited by this method. This technique is ellipsometry.

One of the requirements of the experimental devices is to have a minimum of reflected light. In order to get this it has been necessary to deposit the antireflective coating on a polished silicon wafer without texturization. Due to this fact, the absolute values of thickness are not comparable with the obtained ones by means of electron microscopy.

In Fig. 9, we have represented the thickness of the TiO_2 film versus x and y coordinates of the silicon wafer. One graphic in this figure corresponds to the film "as deposited" (a) and the other to the sample annealed at 810 °C (b). From this figure, we can confirm that the TiO_2 films deposited by APCVD are uniform in thickness. It is interesting to note that the heat treatment produces a contraction in thickness and an increase in refractive index. The last one varies from 1.98 for the "as-deposited" sample to 2.21 for the annealed sample. These results suggest that the film after heat treatment has gone though a densification due to the phase transition from amorphous to partially crystalline anatase.

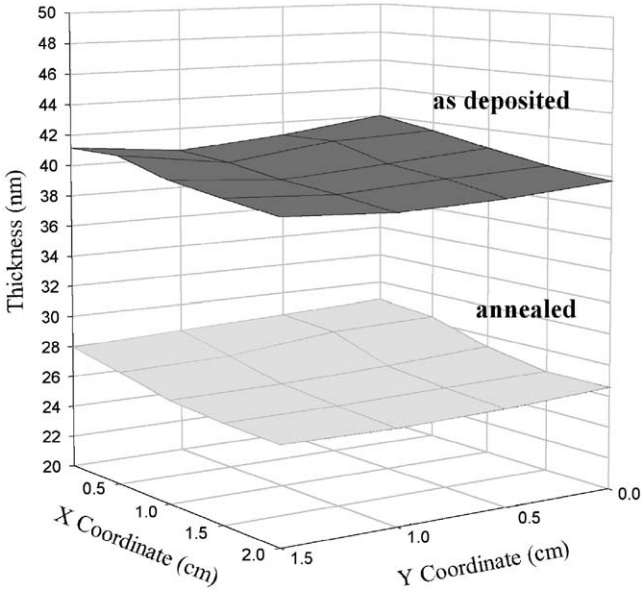

Fig. 9. Thickness of TiO_2 thin films versus surface of the silicon wafer in two cases: "as-deposited" film and after annealing at 810 °C.

4. Conclusions

Antireflective TiO_2 films have been deposited on textured silicon wafer by APCVD. Their structure and morphology have been investigated. The results presented in this paper show the following:

- TEM images exhibit an inhomogeneous contrast; this implies that the deposited layer is inhomogeneous in depth. It presents two zones with different densities, which look like a double layer. The inner layer of this corresponds to an interface of amorphous material; we suggest that it might be constituted by a silicate of the type $TiSi_xO_y$. The outer one corresponds to a TiO_2 layer. The TEM images show that there is no mixing between both layers, the transition from one to another is rather sharp. The formation of the TiO_2 layer occurs when the interface has reached a determined thickness, we have estimated its value to be about 60 nm.
- After annealing at 810 °C, the TiO_2 layer undergoes a phase transition of amorphous to crystalline (anatase phase); however, the interface stays in the amorphous phase.
- The validity of the APCVD has been corroborated as deposition technique of antireflective coating.

Acknowledgements

The authors express their thanks to ISOFOTON for the collaboration. This work has been supported by the 1FD97-0685-C02-01 project with Spain PN I + D funds and UE FEDER program.

References

[1] H. Bach, D. Krause, Thin Films on Glass, Springer, Heidelberg, 1997.
[2] P. Chrysicopoulon, D. Davazoglou, Chr. Trapalis, G. Kordas, Thin Solid Films 323 (1998) 188.
[3] Y.L. Wang, K.Y. Zhang, Surf. Coat. Technol. 140 (2001) 155.
[4] S. Takeda, S. Suzuki, H. Odaka, M. Osono, Thin Solid Films 392 (2001) 338.
[5] G. San Vicente, A. Morales, M.T. Guitierrez, Thin Solid Films 391 (2001) 133.
[6] H.Y. Ha, S.W. Nam, T.H. Lim, I.H. Oh, S.A. Hong, J. Membr. Sci. 111 (1996) 81.
[7] D.C. Wong , A. Waugh, B. Yui, P. Sharrock, First World Conference On Photovoltaic Energy Conversion, 24th IEEE Photovoltaic Specialist Conference Record, 1994, p. 905.
[8] M. Lemiti, J.P. Boyeaux, H. El Omari, A. Kaminski, A. Laugier, Mater. Sci. Semiconductor Processing 1 (1998) 331.
[9] R.J.H Clark, in: S.C. Bailar, H.J. Eneleus, A.F. Trofman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon Press, Oxford, 1973, p. 375.
[10] C.J. Taylor, D.C. Gilmer, D.G. Colombo, G.D. Wilk, S.A. Campbell, J. Roberts, W.L. Gladfelter, J. Am. Chem. Soc. 121 (1999) 5220.
[11] A. Sandell, M.P. Anderson, Y. Alfredsson, M.K-J. Johansson, J. Schnadt, H. Rensmo, H. Siegbahn, P. Uvdal, J. Appl. Phys. 92 (2002) 3381.
[12] A. Sandell, M.P. Anderson, M.K.-J. Johansson, P.G. Karlsson, Y. Alfredsson, J. Schnadt, H. Siegbahn, P. Uvdal, Surf. Sci. 530 (2003) 63.