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Deposition of SiO_2 and TiO_2 thin films by plasma enhanced chemical vapor deposition for antireflection coating

C. Martinet *, V. Paillard, A. Gagnaire, J. Joseph

Département de Physico-chimie des Matériaux, UMR CNRS 5512, Ecole centrale de Lyon, BP 163, 69131 Ecully, France

Abstract

Silicon dioxide and titanium dioxide films were deposited at low temperature by electron cyclotron resonance (ECR) plasma enhanced chemical vapor deposition (PECVD) using respectively O_2 and tetraethoxysilane (TEOS) or titanium isopropoxide (TIPT) as precursors. To control the thickness and the refractive index during deposition, the plasma reactor was equipped with an in situ spectroscopic ellipsometer. Deposition kinetics and layer properties were investigated by spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS) and chemical etch rate. A double film antireflection coating was fabricated and reflectance was measured using a UV-visible near-infrared spectrometer. Results reported demonstrate that deposition of SiO_2 and TiO_2 films at low temperature by PECVD is a promising method to produce antireflection coatings for solar cells. © 1997 Elsevier Science B.V.

1. Introduction

In the area of optics and optoelectronics, transparent dielectrics with different refractive indices are required to produce, for instance, Bragg mirrors [1,2] or antireflection coatings [3,4]. To meet this condition, TiO_2 and SiO_2 appear well suited for applications in a visible wavelength range. Various methods exist to prepare oxide films such as SiO_2 and TiO_2. Among these, chemical vapor deposition (CVD) [5,6] is known to give a large density film, good stoichiometry and uniformity over a large area. However, this method requires a high temperature to produce high quality materials and for many applications the substrate cannot tolerate being heated. Thus, plasma enhanced chemical vapor deposition (PECVD) appears to be more suitable since high quality materials can also be obtained but at lower temperatures. In this study, PECVD using the electron cyclotron resonance (ECR) technique was chosen since its large density plasma produces very good quality dielectrics at room temperature and low pressure [7]. In optics, thickness and film index are important for applications, thus, measurement of these parameters during fabrication appears to be particularly valuable. In this work, these measurements were carried out using in situ spectroscopic ellipsometry during deposition.

The simplest way to obtain an oxide film stack by plasma CVD is to use an O_2 plasma for both materials and to switch only the precursor to produce SiO_2 or TiO_2. This method was used in our study. Precursors for SiO_2 and TiO_2 were tetraethoxysilane (TEOS, $(Si–(OC_2H_5)_4)$ and titanium isopropoxide (TIPT, $Ti(O–i–C_3H_7)_4$). These precursors have several advantages: they are very volatile at low temperatures (50°C minimum) [8], they are non-dangerous

* Corresponding author. Tel.: +33-4 72 18 62 59; fax: +33-4 72 18 60 90; e-mail: martinet@cc.ec-lyon.fr.

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products (as compared to SiH_4) [9] and they are easy to use. Moreover, contamination with TIPT is small, for example less than that with $TiCl_4$, which tends to incorporate chlorine into the film [10]. SiO_2 deposition by PECVD with a precursor such as TEOS has been studied previously [11,12] but TiO_2 deposition by plasma has received little interest until now [13,14].

In this paper, we report our preliminary results on the fabrication of an antireflection coating using the PECVD method. We studied first the effects of deposition parameters on growth and the properties of SiO_2 and TiO_2 films. We then fabricated a double-layer TiO_2/SiO_2 antireflection coating to validate the deposition process. Performance of this coating was evaluated by reflectometry measurements.

2. Experimental description

SiO_2 and TiO_2 films were deposited using the experimental system shown in Fig. 1. The plasma was excited at microwave frequency (2.45 GHz) under the electron cyclotron resonance (ECR) condition (the magnet was just over the antenna to provide the 875 Gauss ECR condition). TEOS vapor was introduced into the reactor chamber through a mass flow controller. O_2 gas was introduced near the microwave antenna. Pressure measured during the process by a baratron gauge was typically 1 mTorr. The sample was placed about 10 cm below the plasma in a plasma diffusion area. Titanium or silicon precursors were introduced via two rings, placed 4 cm above the sample, to provide a homogeneous flow around the sample. These TIPT and TEOS precursors, were heated to around 60°C and feed lines were heated to 100°C to avoid precursor recondensation. Samples were also heated (100°C to 400°C) to avoid product precursor recondensation. No sample polarization was used, so that the sample was at floating potential with respect to the plasma. In this study, substrates were Si(100) wafers.

The reactor chamber was equipped with in situ spectroscopic ellipsometry, a homemade rotating polarizer system, with an incidence angle of 70°. Ellipsometry is based on polarization transformation that occurs when a beam of polarized light is reflected from or transmitted through a medium, the polarization modification is determined by the optical properties (refractive index and layer thickness) of the

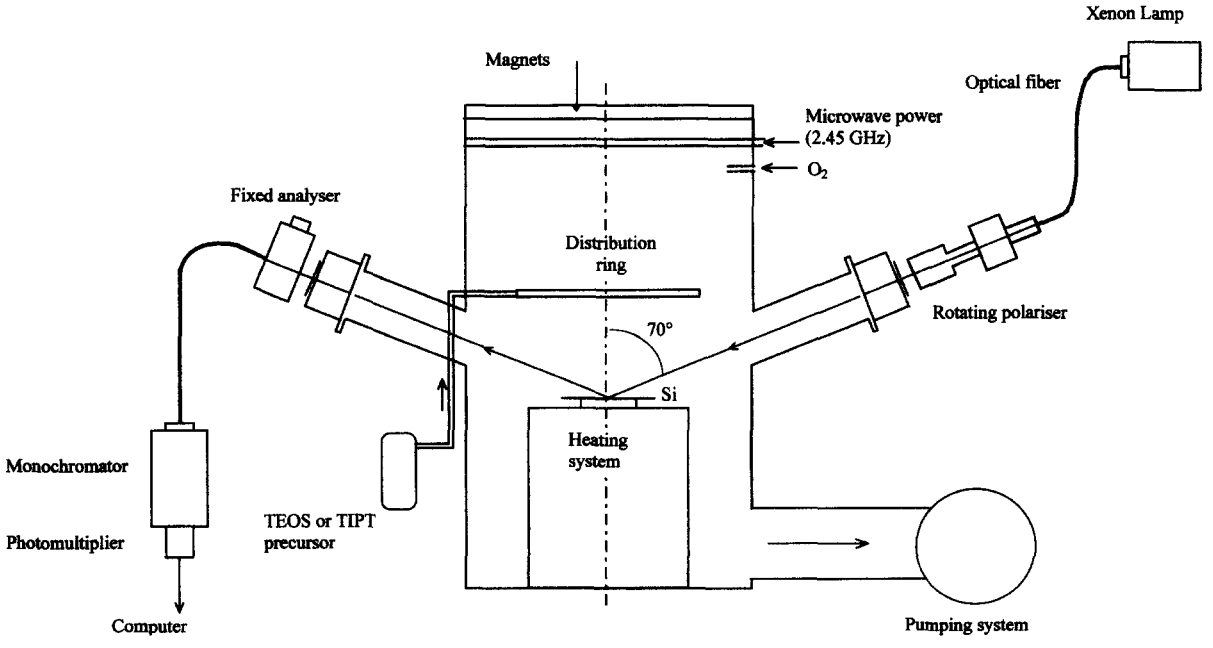

Fig. 1. Experimental set up.

material [15]. Thus, the reflection coefficient consists of two parts: a phase change and an amplitude change. These changes are different for an incident vibration with its electric vector oscillating in the plane of incidence (p-state polarization) compared to radiation with its electric vector oscillating perpendicularly to the plane of incidence (s-state polarization). An ellipsometer measures the ratio of the p-state to s-state Fresnel reflection coefficients:

$$\rho = R_p/R_s = \tan\psi e^{i\Delta};$$

Ψ and Δ are called the ellipsometric angles.

The classical ellipsometric method for in situ control consists of following the trajectory of these ellipsometric angles during the process at a given wavelength. Thus, a Δ versus Ψ curve is plotted in Cartesian coordinates, the film thickness being the variable parameter along the curve [16]. To determine deposition kinetics and the refractive index of a layer from this data, the measured ellipsometry trajectory is compared to the theoretical trajectory obtained from a model [17]. In this work the simplest model was used: one homogeneous layer on a silicon substrate.

For SiO_2 deposition, the 340 nm control wavelength was selected given that at this wavelength the refractive index of silicon (n_{Si}) is independent of the temperature [18], so that we were not concerned with possible uncertainty due to uncertainty in n_{Si}. But for TiO_2, this control wavelength cannot be used because this material absorbs up to 400 nm, therefore measurements were performed at 500 nm.

After deposition, layers were measured using spectroscopic ellipsometry. This measurement yields reliable information on the dielectric function of the layer. The classical method for data reduction lies in comparison of the measured dielectric function with a layer model obtained using the Bruggeman effective medium approximation (BEMA) [19]. In this model, the layer is described as an homogeneous mixture of components. A literature database of refractive indices is used for the known constituents of the film and a minimizing procedure gives both the film thickness and the percentages of constituents. Moreover, measurements taken at different places make it possible to estimate the spatial homogeneity of film thickness.

For SiO_2 films, the etch rate was measured in a buffered etch solution (4% HF in solution). These measurements were carried out and compared to a thermal oxide reference to avoid any dependence on the HF concentration variation of the etching solution. Atomic layer composition (stoichiometry, contamination) was measured by X-ray photoelectron spectroscopy (XPS). The reflectivity spectrum of an anti-reflection coating was measured with a UV-visible near-infrared reflectometer.

3. Results

3.1. SiO_2 deposition

Plasma parameters (TEOS flow rate, temperature, microwave power) were varied to optimize quality of the SiO_2 deposition. Plasma conditions studied for the SiO_2 deposition were: substrate temperature between 100°C and 400°C, TEOS flow between 2.5 sccm and 5 sccm, oxygen flow constant at 8 sccm and microwave power between 50 and 100 W. The deposition process was controlled ellipsometrically [20]. An example of a typical $\Delta(\Psi)$ experimental curve is plotted in Fig. 2. In this figure, measurements are compared to simulations with different refractive indices to show the sensitivity of the mea-

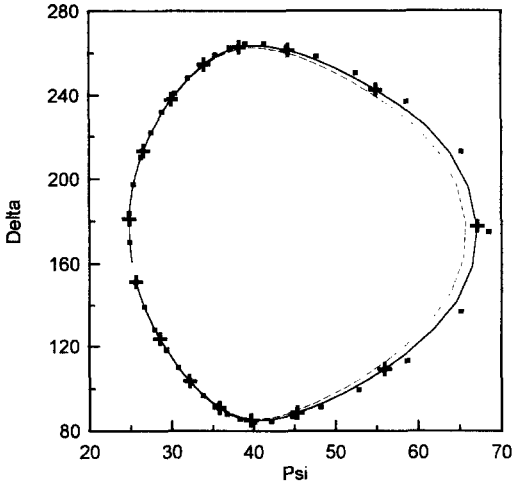

Fig. 2. Experimental evolution of the $\Psi(\Delta)$ trajectory during SiO_2 deposition (crosses). Solids dotted and dashed lines correspond to calculations (dotted line: refractive index of 1.460, continuous line: $n = 1.480$, dashed line: $n = 1.500$).

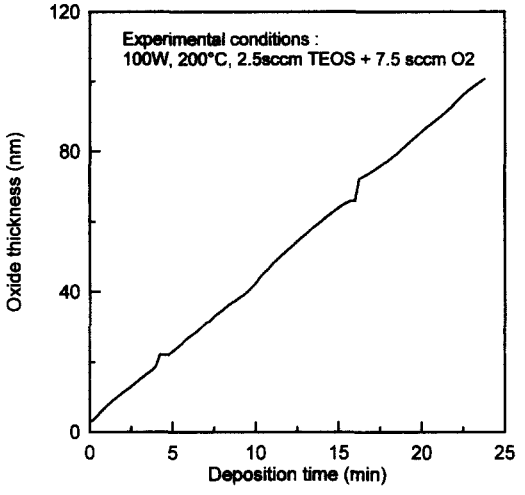

Fig. 3. Thickness of the SiO_2 layer deposited versus time.

surement on the refractive indices of the layer. Adjustment of a theoretical $\Delta(\Psi)$ trajectory to the experimental one allows a plot of the growth kinetics (Fig. 3). This figure shows that the growth rate was constant during deposition. The deposition rate was measured by this method under all deposition conditions, the results are presented in Table 1. Examination of the growth rate shows that it decreases as the deposition temperature increases and the growth rate increases as the TEOS flow increases (Table 1).

After each deposition, the sample was measured by ex-situ spectroscopic ellipsometry to compare the dielectric function of SiO_2 deposition to a reference thermal silicon dioxide [21]. Results showed that the dielectric function was close to reference thermal oxide. Other measurements were performed and their results are summarized in Table 1. XPS measurements show that the SiO_2 layers are stoichiometric with a small concentration of carbon (due to the TEOS precursor) and some impurities from reactor walls (Ni, Fe, Cr, Mo, ...). We also determined the chemical etch rate (HF diluted), by measuring thickness and refractive index by spectroscopy ellipsometry after each etch time. This measurement also confirms that the SiO_2 deposited was homogeneous because it was verified that during etching the thickness removed varied linearly with the etch time. Moreover, the etch rate of the film is ~ 2.5 times greater than that of the thermal oxide.

This study shows that the properties of PECVD SiO_2 deposited layers are similar to thermal oxide properties. Moreover, the results obtained were reproducible (see Table 1).

3.2. TiO_2 deposition

TiO_2 deposition was studied using the same procedure as for the SiO_2 deposition. Typically, plasma conditions used were: 75 W microwave power, 100°C sample temperature, floating potential, 8 sccm O_2 flow (corresponding to 1 mTorr pressure) and 0.5 mTorr TIPT precursor. TIPT flow was adjusted using a needle value, thus only the chamber pressure was measured to control the precursor flow. This pressure was constant during the deposition process. The sample was heated to 100°C to avoid precursor recondensation.

Fig. 4 shows a typical ellipsometric trajectory and Fig. 5 represents the growth curve deduced from this trajectory. This analysis indicates that the layer was

Table 1
Deposition parameters and properties of the deposited SiO_2 films

TEOS (sccm)	Microwave power (W)	Sample temperature (°C)	Deposition rate (nm/min)	Final thickness (nm)	Void in the SiO_2 (%)	Refractive index ($\lambda = 633$ nm)	Etch chemical rate (nm/min)	XPS Stoichiometry O/Si	XPS at.% C/O
2.5	75	200	2.45 ± 0.1	79 ± 0.5	-0.5 ± 0.2	1.459 ± 0.001	16.0 ± 0.2		
2.5	75	200	2.50 ± 0.1	108 ± 0.1	0.07 ± 0.2	1.456 ± 0.001		2.18 ± 0.5	2.03 ± 1.0
3.75	75	200	4.43 ± 0.1	153 ± 0.5	-1.3 ± 0.2	1.463 ± 0.001	13.6 ± 0.2		
5	75	200	6.88 ± 0.1	168 ± 0.5	-1.0 ± 0.2	1.462 ± 0.001		2.00 ± 0.5	0.34 ± 1.0
2.5	100	200	3.16 ± 0.1	116 ± 0.5	-0.3 ± 0.2	1.458 ± 0.001	15.5 ± 0.2	2.08 ± 0.5	1.05 ± 1.0
2.5	75	350	2.10 ± 0.1	87 ± 0.5	-0.1 ± 0.2	1.457 ± 0.001			
Thermal oxide					0 ± 0.2	1.457 ± 0.001	6.5 ± 0.2		

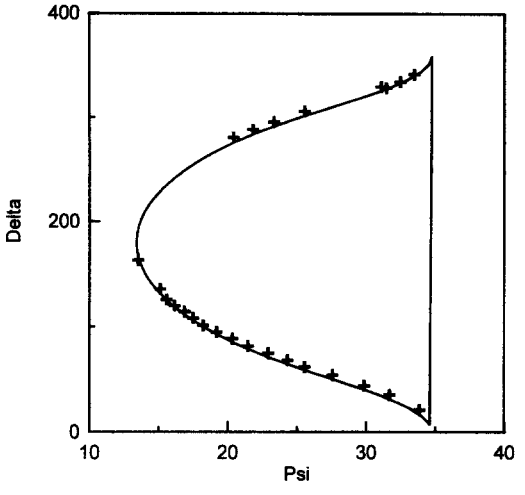

Fig. 4. Evolution of the $\Psi(\Delta)$ trajectory during TiO_2 deposition (crosses). The solid line corresponds to calculation.

homogeneous and transparent at this wavelength (500 nm).

In this work only the TIPT precursor flow was varied, showing that the growth rate increases (1 to 18 nm/min) when the TIPT precursor pressure increases (respectively: 0.1 to 0.25 mTorr). This result proves that the rate was controlled by the precursor flow. When the growth rate increased from 1 to 18 nm/min, the refractive index at 500 nm decreased from 2.38 to 2.1.

After each deposition, the sample was measured by spectroscopic ellipsometry to determine the dielectric function. Using BEMA, this dielectric function was correctly represented with only two components, void and reference TiO_2 [22]. Atomic concentrations were measured by XPS. These measurements showed that the films were contaminated by 13% carbon and that the oxygen concentration was larger than stoichiometric. This analysis also revealed the presence of O–H bonds.

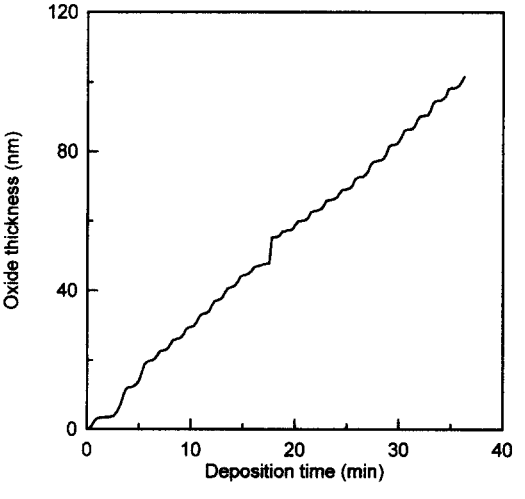

Fig. 5. Thickness of the TiO_2 layer versus deposition time.

4. Applications to antireflection coatings

The above results show that it is possible to fabricate SiO_2 and TiO_2 layers with the optical qualities required for optics. Moreover, film thickness can be easily controlled by insitu ellipsometry. In order to validate the process and the choice of the materials, we have fabricated a double layer anti-reflection (AR) coating for solar cells. Optically, a solar cell uses silicon as a photon absorber but the high refractive index of silicon causes a high reflectivity. Thus an AR coating is used to improve the efficiency of silicon solar cells [23,24]. A single layer can be used (for instance on silicon), an anti-reflection condition at one wavelength can be achieved with only TiO_2. However, to increase the anti-reflection range, additional films are required. With two films, best results are obtained with two quarter-wave films with an index determined from the following equations [25]:

$$n_1^3 = n_0^2 n_s \quad \text{and} \quad n_2^3 = n_0 n_s^2, \tag{1}$$

where n_0 is the refractive index of ambient (air), n_s is the substrate index and n_1, n_2 are respectively the indices of the first and second layer. Moreover, the thickness (e) of each film have to satisfy the relation $ne = \lambda/4$ (quarter-wavelength optical path) due to destructive interferences phenomenon.

For silicon $n_s = 3.95$ at 600 nm, Eq. (1) yields $n_1 = 1.58$ and $n_2 = 2.5$. With SiO_2 as the small index material and TiO_2 as the large index material we can approximately meet these ideal conditions. Furthermore, by adjusting the thicknesses of the two films, a minimum reflectance can be produced. In this study, we chose to minimize reflectance around the 0.7 μm wavelength. Taking into account the refractive indices of the TiO_2 and SiO_2, films, a thickness of 72 nm for a bottom TiO_2 layer and a

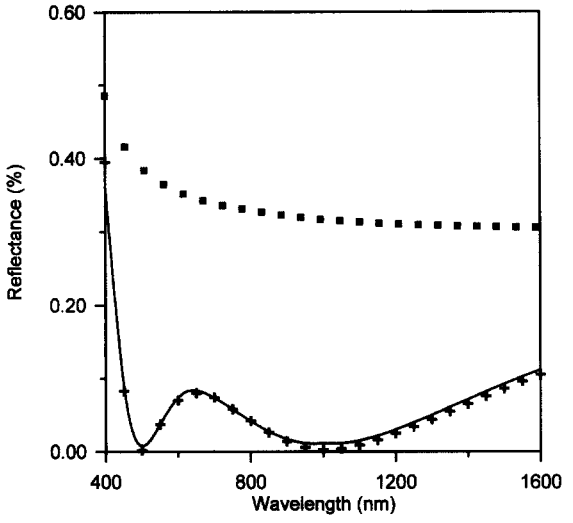

Fig. 6. Reflectivity versus wavelength for a bare silicon substrate (squares) and with an antireflection TiO_2/SiO_2 coating (crosses). The solid line corresponds to calculation.

thickness of 107 nm for the top SiO_2 layer were obtained from the above equations.

For layer fabrication, classical plasma conditions were used: 100°C for deposition temperature, 8 sccm for O_2 flow, 75 W microwave power. The coating obtained was measured by spectroscopic reflectance and compared with the measurement of a bare silicon substrate. Results presented in Fig. 6 show the important reduction of reflectance between a silicon substrate and a TiO_2/SiO_2 double layer AR coating and the good agreement between experimental measurement and calculation from TiO_2, SiO_2 thicknesses determined by in situ ellipsometry.

5. Conclusion

The results reported show that materials fabricated by PECVD can be obtained having optical properties required for coatings. Moreover, the use of in situ ellipsometry makes it possible to monitor the layer during deposition. This measurement is well adapted to coatings since it allows control of the two crucial parameters: thickness and refractive index of the layer. The fabrication of a double layer antireflection coating validates the choice of the materials and the method used for their fabrication. SiO_2 and TiO_2 deposited respectively from TEOS and TIPT precursors at low temperature can be used for optical application.

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