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A soft Plasma Enhanced-Chemical Vapor Deposition process for the tailored synthesis of SiO_2 films

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Abstract

The availability of soft synthetic processes for the preparation of SiO_2 films with tailored features plays a key role for several technological applications, from optics to electronics, from surface modifications to barrier coatings. In such context, this work presents the development and optimization of a Plasma Enhanced-Chemical Vapor Deposition route towards high-purity SiO_2 films at near room temperature. Depositions were performed from Ar and Ar–O_2 plasmas using tetramethoxysilane as precursor, devoting particular attention to the interplay between film properties and process parameters (RF- (Radio Frequency-) power, total pressure, $O_2/(Ar+O_2)$ ratio and precursor vaporization temperature). Real-time information on the growth process was gained by Laser Reflection Interferometry, while the chemical composition and bonding structure of the obtained layers were analyzed by Fourier Transform Infrared Spectroscopy and X-ray Photoelectron Spectroscopy. Scanning Electron and Atomic Force Microscopies were adopted to analyze the surface and cross-sectional film morphology. The system structural and optical properties were investigated by means of Glancing Incidence X-Ray Diffraction and UV–Vis spectroscopy. Finally, nanoindentation measurements were performed to investigate film hardness. Under optimized conditions, very pure silica films, characterized by a remarkable optical transparency and favorable mechanical properties, were obtained even at RF-power values as low as 5 W and in the absence of O_2 in the plasma.
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1. Introduction

The great importance of silicon dioxide (SiO_2, silica) films in many applicative fields, such as optics, optoelectronics and surface modification of polymeric and metallic substrates, has been widely recognized and documented [1–9]. To this regard, the increasing demand for materials and devices with improved performances requires the growth of silica films with electrical, optical, and mechanical properties tailored according to their specific technological utilization [4,10–12]. Furthermore, in the fabrication of multi-layer architectures, an important aspect is that the deposition of each component needs to be compatible with the overall production process, in order to prevent undesired alterations of the system structure and functional performances [6,8,13,14]. To this aim, the deposition of SiO_2 films with precise chemico-physical characteristics (such as high purity, high optical transparency, thickness homogeneity) under soft preparation conditions is highly desirable and still represents a strategic goal despite the extensive research activities on the topic. To this regard, Plasma Enhanced-Chemical Vapor Deposition (PE-CVD) is one of the most appealing techniques for its remarkable versatility in terms of process control. Among its important advantages with respect to other routes [11,15–17], the low deposition temperature and the peculiar activation provided by non-equilibrium plasmas [18,19] enable the use of softer operating conditions in terms of energy supply and reaction atmosphere, thus minimizing diffusion phenomena, interface reactions and segregation effects [11,20]. Such features, in turn, allow to preserve the chemical identity of the different multi-layer

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components, as well as their morphology, thus permitting deposition even on thermally-sensitive substrates [6,9,12].

In this context, the present work is the initial part of a research activity devoted to the preparation of multi-layer systems, based on silica films and ordered arrays of metal nanoparticles (NPs), for optical and optoelectronic applications. To this aim, silica deposition has to be optimized in order to avoid structural and morphological modifications of the underlying metal NPs, since the system functional performances strongly depend on the NPs size, shape and distribution [21,22]. It is worth noting that silica does not constitute a mere passive encapsulating layer, since its chemico-physical characteristics influence, in turn, the overall architecture properties. The above applications require a careful control of the SiO_2 film purity and thickness, as well of its mechanical and optical properties (hardness, adhesion, transparency, roughness…).

Basing on the above considerations, the main goal of the present work is the development and optimization of a synthetic protocol for the deposition of SiO_2 films at temperatures as low as 60 °C and under mild plasma conditions. Experiments were performed from Ar and Ar–O_2 plasmas, devoting particular attention to the influence of RF-power, total pressure, $O_2/(Ar+O_2)$ ratio, and precursor vaporization temperature. Tetramethoxysilane (TMOS) was chosen as precursor compound for its favourable characteristics [23]. Si(100), silica slides and polished copper discs were used as substrates for an extensive chemico-physical characterization of the deposited films. The simultaneous use of RF-power and deposition temperatures as low as in the present work has never been reported in the literature up to date for the PE-CVD of silica films.

2. Experimental details

2.1. Synthesis

Silica deposition was performed at 60 °C from Ar and Ar–O_2 plasmas by means of a two-electrode custom-built instrument (ν=13.56 MHz) described elsewhere [18]. Si(100) wafers (MEMC®, Merano, Italy), commercial SiO_2 slides (Heraeus, Hanau, Germany) and polished copper discs were used as substrates. Before each experiment, substrates were cleaned according to a well-established procedure [23] in order to remove surface contaminants. TMOS (99+%), purchased from Aldrich® and used without further purification, was vaporized at 0 and −18 °C by means of suitable cooling baths. The influence of RF-power (varied from 5 to 20 W) was investigated at total pressures of 100 and 200 Pa. The $O_2/(Ar+O_2)$ ratio in the plasma was calculated by the formula:

$$R(O_2) = \Phi(O_2)/[\Phi(O_2) + \Phi(Ar)] \quad (1)$$

where $\Phi(O_2)$ and $\Phi(Ar)$ are the O_2 and Ar flow rates, respectively. In the present work $R(O_2)$ was varied between 0 and 0.30.

2.2. Characterization

Laser Reflection Interferometry (LRI) measurements were carried out using a He–Ne diode laser (λ=670 nm) incident on the substrate at an angle of 70° from the normal. The light reflected by the growth surface was collected by a PIN diode and the signal was digitized and recorded vs. time by a computer [21].

Fourier Transform Infrared Spectroscopy (FT-IR) spectra were obtained by means of a Jasco VIR 9500 instrument operating in transmittance mode at normal incidence.

X-ray Photoelectron Spectroscopy (XPS) analyses were performed by a Perkin Elmer Φ 5600ci spectrometer with a non-monochromatized AlK_α (1486.6 eV) source, at working pressures lower than 10^{-7} Pa.

The reported Binding Energy (BE) values (standard deviation=±0.2 eV) were corrected for charging by assigning a BE of 284.8 eV to the C1s line of adventitious carbon [24]. The atomic compositions were evaluated using sensitivity factors provided by Φ V5.4 A software. Sputtering treatments were carried out using an Ar^+ beam at 2.5 kV, with an argon partial pressure of 5×10^{-6} Pa and a rastered area of 2×2 mm^2.

Scanning Electron Microscopy (SEM) measurements were carried out by means of a Field Emission Zeiss SUPRA 40VP instrument. Surface and cross-sectional images were acquired adopting an accelerating voltage between 10 and 20 kV.

A NT-MDT SPM Solver P47H-PRO instrument was used for Atomic Force Microscopy (AFM) measurements. Areas of 1×1 μm^2 were scanned in tapping mode in air. After plane fitting, the Root Mean Square roughness (RMS) was calculated from the height profile by the following relation:

$$\mathrm{RMS} = \left[\sum (z_i - Z)^2/n\right]^{1/2} \quad (2)$$

where z_i, Z and n represent the local height, the mean height and the number of data points, respectively [17].

Glancing Incidence X-Ray Diffraction (GIXRD) patterns were recorded using a Bruker D8 Advance instrument equipped with a Göbel mirror and a CuK_α source (40 kV, 40 mA) in the 10–50° 2ϑ range, at a fixed incidence angle of 0.5°.

Optical absorption spectra were recorded on SiO_2-supported samples in transmittance mode by a Cary 5000 UV–Vis–NIR (Varian) spectrophotometer in the range 200–800 nm (spectral bandwidth=1 nm).

Nanoindentation measurements were performed by a Nanotest 600 instrument from Micromaterials Ltd with a pyramidal diamond indenter. The hardness values were determined from indentation curves with a loading ranging from 0.5 to 30 mN, as previously described [20].

3. Results and discussion

The first part of this work was devoted to evaluating the combined influence of the $O_2/(Ar+O_2)$ ratio [$R(O_2)$] and the applied RF-power on the precursor decomposition pathway and film growth rate. To this regard, valuable information were obtained by LRI, an *in-situ* diagnostic tool compatible with the reactive PE-CVD environment, allowing the real-time investigation of the deposition process and film thickness control [21,25]. Up to date such a technique has never been applied for the monitoring of silica growth by PE-CVD. Fig. 1 reports the

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