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Effect of the Substrate Nature on the Structure and Optical Properties of Amorphous Silicon Nanoparticles Embedded into Porous Anodic Aluminum Template

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Abstract

In this paper, we considered fabrication of amorphous silicon nanoparticles (a-Si Nps) on porous anodic aluminum template, and influence substrate nature on them. In our case, the porous anodic aluminum films (PAL) were prepared by two-step anodization technique on different substrates (e.g., glass, aluminum and stainless steel), and followed by deposition of a-Si:H thin films at lower substrate temperature (150°C). The influence of substrate on the structural and optical properties of these samples (as labelled PALSi) was investigated through an extensive characterization. The microstructure of the PAL layer and a-Si:H films was systematically studied micro-Raman, X-ray photoelectron, Fourier transform infrared spectroscopies and scanning/transmission electron microscopies analyses. The optical constants (n and k as a function of wavelength) of the films were obtained using variable angle spectroscopic ellipsometry (SE) in the UV–vis–NIR regions. The deposited film was modeled as a mixture of void, amorphous silicon and aluminum using the Bruggeman approximation. Based on this full characterization, it is demonstrated that the optical properties of the films are directly correlated to their micro-structural properties, which are strongly dependent on the nature of substrate.

Keywords: Amorphous silicon nanoparticle; Plasma enhanced chemical vapor deposition (PECVD); Hydrogenated amorphous silicon; Porous anodic aluminum; Substrate

Introduction

In the last decades the Researchers have been focused on nanostructured porous materials because of their unique geometrical properties. Such nanoporous materials are very suitable as a template for synthesis of functional nanostructures [1,2] or they can be also used for fabrication of various nanodevices, e.g., solar cells [3,4], photonic crystals [5,6] or magnetic storage [7].

During the last few years, the elaboration of porous aluminum structures by anodization of thin Al on different substrates have attracted considerable attention as nanostructural dielectric templates, which allow depositing metal [8-10], semiconductor [11,12], carbon nanotube [13] and conductive polymer [14] particles of controlled size and morphology.

In most cases, Si wafers are used as substrates for the deposition of thin Al films [15-17]. Depending on the purpose of the final PAL structures, intermediate (e.g., conductive) layers can be introduced [18,19]. More recently, the elaboration of PAL films by anodization of Al thin films on different substrates (in our case, glass, aluminum, stainless steel) have been extensively fabricated [20]. We have demonstrated that the self-organization of the pores is highly dependent on the morphology of the substrate-type.

In this work we demonstrate the possibly to grow of nanostructures Si (e.g., nanoparticles) embedded into the PAL templates formed, at room temperature, on three substrates (glass, aluminum and stainless steel). An amorphous silicon films are deposited by a PECVD technique. A film growth rate up 2 A°/s has been achieved. The Spectroscopic E spectra are measured in the range of 200-850 nm with a rotating polarizer ellipsometer. The PALSi was modeled as a mixture of void, aluminum and amorphous silicon or fine grains embedded in amorphous matrix. The complex refractive index n(E) and extinction

coefficient k(E) of the a-Si layer are calculated using the Bruggeman approximation [21]. The optical properties of the deposited films are correlated to the porous aluminum and a-Si films nanostructure. The energy gap of the a-Si films depends strongly on the porosity.

Experimental Section

Synthesis of a-Si:H embedded into porous anodic aluminum (PALSi)

The 2 µm-thick of aluminum of (99.99%, high purity) was evaporated on the following substrates: aluminum alloy, glass and stainless steel. All substrates were cleaned by acetone and ethanol to remove contaminants from their surface. Then, the porous alumina layer (PAL) was formed by two-step anodization as described in our previous works [20]. Then, the a-Si:H films were deposited by the plasma-enhanced chemical vapour deposition (PECVD) on the porous anodic aluminum layer (PALSi) at 150°C, using a gas mixture of silane and H₂ at a total pressure of 0.5 mTorr.

Characterization techniques

The Raman spectroscopy was performed to know the structure of

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the deposited a-Si:H thin films. Morphological characteristics of the deposited PALSi films on different substrate have been investigated using Scanning Electron Microscopy (SEM), a scanning electron microscope (FESEM, ZEISS-Merlin with Gemini II_ column) with an acceleration voltage of 1.5-3 kV and at a working distance of 3.5-5.5 mm. The presence of silicon nanoparticles was detected by transmission electron microscopy (TEM).

The relative atomic content and the bonding configurations in the surface films were investigated by X-ray photoelectron spectroscopy (XPS). The analysis were acquired using a K-Alpha system of Thermo Scientific, equipped with a monochromatic Al-K α source (1486.6 eV), and operating in constant analyzer energy (CAE) mode with a spot size of 400 micron. Fourier transform infrared spectroscopy (Perkin-Elmer FTIR spectrophotometer) was performed to determine the type amount of the hydrogen bonds.

The optical properties of PALSi films were acquired using variable angle spectroscopic ellipsometry (SE). The ellipsometric angle Ψ and phase difference were measured as a function of wavelength and angle of incidence. The measurements were performed in the wavelength range of 300-800 nm, using an angle of incidence varying from 50° to 80° by steps of 5°. A compensator plate was used with the rotating analyzer configuration to improve phase measurement accuracy over a full 360° range. When used with an appropriate optical model describing the optical dispersion of the sample and its spatial structure (in our case a-Si:H thin films deposited on porous aluminum layer), SE allows accurate determination of film thickness as well as refractive index dispersion n(E) and extinction coefficient k(E) as functions of photon energy E (or wavelength). n(E) and k(E) were calculated in the case of PALSi thin films using the Bruggman model.

The thickness of the films was determined by DEKTAK thickness profilometer estimation.

We show that the thickness of the PALSi films is similar for the different samples (at about 50 nm and 40 nm for the a-Si:H thin film and the PAL layer respectively).

Results and Discussions

SEM and TEM analyses

In Figure 1 are shown SEM images of the PALSi films grown on the

different substrates at the substrate temperature of 150°C. It is evident that, for the same synthesis procedure, the morphology of the samples is very different.

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For the sample grown on glass, the surface is characterized by islands, result of the coalescence of Si nanoparticles. The sample grown on aluminum exhibits a rather smooth grainy surface. The grains have spherical or oval shape and are almost uniform in size.

Furthermore, the film grown on stainless steel consists of smaller grains and there are more big hillocks on the surface.

These smaller grains (about 3 nm in size) are organized in a welldefined geometry as nanoparticles injected the porous aluminum layer, as shown by TEM image (Figure 2).

Raman and FTIR analyses

Figure 3 shows the Raman spectra of the different a-Si:H thin films deposited on porous anodic aluminum (PAISi) by PECVD technique under the same condition, but on different substrate-type. These spectra are characterized by a broad peak located around 475 cm⁻¹ corresponding to TO phonon mode and the vibration density states characteristic of amorphous Si as well-known since Iqbal and Veprek [21]. No noticeable Raman shift is observed for all samples, indicating that the a-Si:H thin films remain amorphous at different substrate-type.

Therefore, Figure 3 shows the Raman peak observed around 625 cm⁻¹ caused by the presence of hydrogen in the film and corresponds to wagging vibration of Si-H bonds [22].

Figure 4 displays the FTIR absorption spectra of the all synthesized samples. Several vibration bands can be found in the 400-2500 cm⁻¹ region.

The change observed in the form of the FTIR spectra as a function of substrate is related to the effect of substrate on the FTIR analysis in reflection mode.

Several absorption peaks associating to the different vibration modes of the bonds between Si, H and O can be found in the 400-2500 cm⁻¹ region.

The vibration band at about 460 ± 5 , 950 ± 5 and 1100 ± 10 cm⁻¹, for different substrates, are related to rocking, bending and stretching





modes of Si–O–Si, respectively [23]. The enhanced intensity peak at 1100 cm⁻¹ indicates that the layer has a porous structure with a significant decrease in size of Si nanoparticles [24]. This indicates the in-diffusion of oxygen into the films. This result is confirmed by

TEM analysis in Figure 3. The absorption band centered at about 620 cm⁻¹ is associated to the rocking/wagging modes of Si-H_n bonds mainly in the monohydride configuration, typical of less disordered or microcrystalline materials [25,26]. The absorption peak at 620 cm⁻¹ was

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used to determine the total hydrogen content, C_{H} , using the following relation:

$$C_{H=}A * I/N$$

where A_{620} =1.6 *10¹⁹ cm⁻² and N=5.0 *10²² cm⁻³, being N the atomic number density of pure silicon. The estimated hydrogen contents are: 2.69 %, 2.76 % and 3.87 %, for the PALSi grown on aluminum, glass and stainless steel substrates respectively. This indicates that the indiffusion of the impurities, particularly the oxygen, into the film grown on the stainless steel is less than the other substrates.

XPS analysis

In Table 1 are shown the atomic percentages of all the collected species, for the deposited a-Si on PAL grown on different substrates: aluminum, glass and stainless steel. The different samples were analyzed before and after removing of about 3 nm of deposited films by Ar+ etching treatment.

Similar trends are found for the all synthesizes samples prepared on different substrates. The surface of the deposited a-Si:H thin films are mainly composed by silicon, oxygen and carbon. Hydrogen atoms are not detected by XPS analysis.

The presence of the large amount of oxygen element (about 30%) may be come from two contributions; the most part from the surface contamination under atmosphere after long time the deposition, and the second part from the O obtained in the fabricated PAL layer.

While, the presence of C (about 15-20%) may comes from the different electrolytes acid used in the synthesis of the PAI layer [20].

Therefore, after the etching of about 3 nm, we show a rapid increase of the silicon atomic percentage (up to 80-90%), as well as a significant decrease of the silicon and carbon content.

In order to investigate about the changes of the bonding configurations as a function of the substrate-type, XPS acquisitions of all the collected atomic species at high resolution (HR) were carried out.

Figure 5 shows high resolution XPS spectra of Si2p peaks, taken before (A) and after (B) Ar^+ etching for all investigated samples. There is no observable difference comparing all the studied samples. The Si2p XPS spectra are characterized by the presence of two features, generally ascribed to the metallic and oxide phases, located at about 99.5 eV (Si0) and 104.5 eV, respectively (Figure 5) [27]. Instead, after the removal of about 3 nm of materials, Si 2p spectra show the disappearance of the Si-Ox and SiC bonding contribution (Figure 5)

For more detail, the haute resolution Si2p core line was deconvoluted using Gauss-Lorentzian subbands and a Shirley-type background function (Figure 6), taking into account of both the oxygenated and carbidization of the silicon phases [28].

The spectra decomposition reveals the presence of three distinct components as seen in Figure 6.

The bands, centered at 99.5, 100.5 and 104.5 eV originate respectively from metallic like silicon, the Si-C and Si-Ox bonding contributions.

The presence of the Si-C bonds on the surface of the silicon films, is attributed to the diffusion of the carbon atoms from the porous

Sample	Aluminum		Glass		Stainless Steel	
Atomic percent (%)	before etching	After etching	before etching	After etching	before etching	After etching
Si	56.51	91.15	49.04	84.47	47.19	81.77
0	28.05	2.67	32.11	7.1	30.15	7.94
С	15.18	1.853	16.9	3.25	20.89	4.85
AI	0	0	0.29	0.69	1.01	0.82



Table 1: Atomic percentages for different samples before and after removing of about 3 nm of deposited films by Ar+ etching treatment.



aluminum (vary from 25 to 35% at as a function of substrate-type [20]) to the surface during the deposition of a-Si:H thin films and it's proved by C1s core level, located in the 280-290 eV binding energy range.

C1s lineshape was deconvoluted using six contributions. The band at 283.5 eV refers to C-Si bonds, the main contribution at 284.5 eV is attributed to C=C/C-C in the aromatic ring and four other contributions at higher binding energies corresponding to carbon atoms bonded to oxygen in different surface functionalities (C-OH, C-O,C=O) centred at 285.8, 286.6 and 287.7 eV, respectively. The contribution at 288.3 eV refers to π - π bonds. These results are in good agreement with literature [28].

This means that the untended oxygen incorporated into the film can be considered as structural defects of the silicon thin films. While, the incorporated-carbon is not strongly affected on the structure of a-S:H thin films, indeed, the main bonding contribution is attributed to C=C/C-C.

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Optical properties

To examine the influence of these microstructural characteristics on the optical properties, we performed SE measurements of the PASL produced structures.

To determine the refractive index (n(E)) and extinction coefficient (k(E)), we considered that the PASL layers are inhomogeneous, as shown above by XPS analysis.

The optical properties of the films were determined using the

Bruggeman model based on the equations [21] described below.

$$\sum f_i \, \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} = 0$$

Where f_i is the volume fraction of the materials, ε is the effective dielectric function of the composite material, ε_i is the dielectric function of the materials in their pure forms. The two main components of the Bruggeman model are silicon and aluminum.

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The model is based on additive contribution from each phase into the effective polarisability of the medium [21].

The proposed model is considerate as a mixture of four layers as depicted in Figure 7.

It comprises of a native oxide (SiO) layer, a diffusion layer (SiC) and a blending of a-SiH, Al and void. Here the presence of the SiO in the first layer is to take account the possible formation of a native oxide layer, due to the surface contamination of the PASL structure under atmosphere, while, the diffusion of the carbon atoms from the porous aluminum layer formed in oxalic acid to the surface possible formation of a SiC layer and it is proved by XPS and FTIR spectra. The measured and the best fit ellipsometric spectra for the different samples are shown in Figure 8. This means that the agreement between the fitted and the measured spectra is very good and the approximation of this model can be applied.

Figure 9 shows the refractive index and extinction coefficient as functions of wavelength for the PASL films deposited on different substrates. From Figure 9 we can clearly observe the change in both of refractive index and extinction coefficient with the modifying of the substrate-type.

For example for λ =700 nm the refractive index was about 1.59 (for glass substrate), 1.61 (for aluminum substrate) and 1.62 (for stainless steel substrate). In agreement with the structural and morphological results, we verify that the refractive index value, for a given wavelength, depend in porosity density (void). This can be explained by the distribution and/or nucleation of the silicon aggregates inside the pores of PAL layer, which are strongly dependent on the nature of substrate [20].

The energy band gap was obtained from the relation between the absorption coefficient (α) and extinction coefficient (k), $\alpha = 4k\pi/\lambda$, that have been determined from SE data. (αhv)^{1/2} versus (hv) can be estimated using the Tauc plot method [28]. Figure 10 shows the energy band gap for different samples as a function of the nature of substrate.

The band gap energy of PALSi films is found to be e.g.,=2.13, 2.14 and 2.23 eV for the aluminum, stainless steel and glass substrates respectively. This result can be explained by the oxygen and carbon, quantum size and the amorphous state effects take place in the former

Native oxid	de (SiO)	
D:02 : 1 (0)		
Diffusion layer (Si	1C)	
a-Si:H/ Al/void		
a-Si:H/void/Al		
substrate		
substruct		





particles. So oxygen and carbon diffusion in a-Si:H thin films at the deposition process, can be related to saturation dangling bonds atoms of silicon as shown by the XPS analysis.

Based on the band gap energy obtained for the different samples, we can show that the optical absorption properties are significantly affected by the presence of Si particle with very small size along the pores of PAL (as shown by TEM analysis).

Conclusion

Efficient a-Si:H thin films based optoelectronic device require the development of high quality amorphous Si nanoparticles incorporated into the regular pores of PAL layer which can be produced by using an appropriate substrate. In this work, the nanoparticles silicon thin films

were deposited by PECVD technique on a porous anodic aluminum prepared by anodization of Al thin films on different substrates (glass, aluminum and stainless steel). Well grown films are found along all the substrates but change is observed in the structural and optical properties with the variation of substrate. It was observed that the nanoparticles are organized in well-defined geometry for the samples deposited on glass. The final microstructure of the prepared film depends strongly on the nature of the substrate. Evolution of optical properties (refractive index, extinction coefficient and gap energy) has been analyzed.

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