Short communication

The surface modification of nanoporous SiO$_x$ thin films with a monofunctional organosilane

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Abstract

The surfaces of nanostructured, porous SiO$_x$/Si (air-oxidized Si) and SiO$_x$ thin films, deposited by excimer laser ablation in He and He + O$_2$ gas ambients, respectively, have been modified by the deposition of a monofunctional organosilane. They were characterized using photoacoustic Fourier-transform infrared (FTIR) X-ray photoelectron (XPS) spectroscopies, and field-emission scanning electron microscopy (FESEM). Photoacoustic FTIR analysis indicates that the organosilane has hydrolyzed to form a silanol, which has chemically reacted with SiO$_x$ through its surface silanol (–SiOH) group, to form siloxane (Si–O–Si) structures. An enhanced IR spectral signal is found, due to the expansion and contraction of both the pores of the solid and the gas within them.

Porous silicon is a well-characterized, versatile, inorganic material usually produced through galvanostatic, chemical or photochemical etching procedures, in the presence of HF [1]. It has been intensely studied due to its strong visible light emission (photoluminescence, PL) at room temperature. Because porous silicon is easily prepared from the same single-crystal silicon wafers used in the microelectronics industry, it seems ideal for use in Si-based optoelectronics technologies [2]. However, commercial devices are still not available, due to the lack of PL stability. Much experimental evidence [see, e.g., 3–5] has shown that the PL peak position and intensity are strongly dependent on surface chemistry. Due to the high surface:volume ratio of porous Si, an understanding of the dependence of the PL on the surface chemistry is important for commercial application.

Because porous Si is exposed to air subsequent to manufacture, its surface, at least, is oxidized to SiO$_x$, where $x \leq 2$. Many studies have been carried out on

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bonding to the underlying unoxidized Si; these have recently been reviewed [4], along with studies on bonding to the oxide. Some of these studies intentionally oxidized the surface [4] to facilitate reaction with organosilanes, which have the general formula $Z–(CH_2)_n–Si–(R)_x(OR')_{3-x}$, where $Z–$ is a specially chosen reactive group and R, R' are alkyl groups. Reaction with water leads to the replacement of the $–OR'$ groups with $–OH$. The surface modification and functionalization of porous Si has been found to offer an effective means of improving reaction with biomolecules, such as enzymes [4,6], which may react with the Z– component of the deposited organosilane.

Organosilanes for which $x < 2$ are known to copolymerize [7], ultimately leading to the deposition of multilayer thin films, several nanometers thick, due to the hydrogen bonding of –OH groups; the outer surfaces of these films then contain both Z– and –OH groups, and the Z– groups may then enter into further reaction. The use of an organosilane with $x = 2$, as in the present case, can only lead to the deposition of a monolayer, at most, because the organosilane can either dimerize or deposit onto the substrate, but not both.

Here, we use nanoporous SiO_x/Si and SiO_x thin films, deposited by the laser ablation of a Si target in He and $He + O_2$ gas ambients, respectively, with subsequent exposure to air. This process leads to the deposition of films of self-supported nanoparticles having relatively narrow size distributions [8,9]; in our case, the extent of porosity is controlled through the He gas pressure [10]. Our initial purpose was to functionalize the surfaces of these materials, using the amine-terminated organosilane, γ-aminopropyl dimethyl silanol (subsequent to hydrolysis), as the functionalizing reagent; such functionalization also acts as a stabilization, reducing the number of surface groups capable of participating in further oxidation. Amine-terminated organosilanes have been used extensively in the modification of, e.g., silica gel [11–13], since the amine group offers the possibility of electrostatic, H-bonding and hydrophilic interactions with the amino acid residues of protein molecules. Such systems have application as nanoporous biological sensors [4].

Thin film preparation was carried out in a specially built laser deposition system, with a base pressure of 2×10^{-7} Torr. Experimental details for the production of nanostructured, porous SiO_x/Si and SiO_x thin

films are found elsewhere [14]. Briefly, a pulsed KrF laser (λ = 248 nm, with a pulse period of 20 Hz and a FWHM of 20 ns) was used to ablate an n-type Si wafer, using (i) He, followed by air exposure, to obtain SiO_x/Si and (ii) $He + O_2$ to obtain SiO_x. The laser had a radiation intensity of about 5×10^8 W/cm^2, and was focused at a 45° incident angle, to give a 2 mm × 1 mm spot on a target rotating at 3 rps.

X-ray photoelectron spectroscopy (XPS) was carried out in a VG ESCALAB 3 Mark II, using non-monochromated Mg Kα X-rays (1253.6 eV). The base pressure in the analysis chamber was $<10^{-10}$ Torr. High-resolution spectra were obtained at a perpendicular take-off angle, using a pass energy of 20 and 0.05 eV steps. All peaks were calibrated to adventitious carbon, setting its C1s peak to 285.0 eV.

Photoacoustic Fourier-transform infrared (FTIR) spectra were obtained, using a He-purged MTEC 300 photoacoustic cell, in a Bio-Rad FTS 6000 spectrometer, at a spectral resolution of 4 cm^{-1}. The 5 kHz modulation frequency probed the entire sample thickness.

The organosilane used, γ-aminopropyl dimethyl ethoxysilane, $H_3N–(CH_2)_3–Si(CH_3)_2–OC_2H_5$, was purchased from Gelest; on exposure to water, the ethoxy group ($–OC_2H_5$) hydrolyzes to a hydroxyl group ($–OH$). The organosilane was dissolved in deionized water, 1% v/v, immediately prior to use. After stirring the solution for several minutes, the nanoporous Si thin films were immersed for times ranging from a few seconds to 30 min, followed by gentle washing in deionized water. The modified samples were then dried at room temperature, either under mechanical pump vacuum for 2–3 days or in air, for more than 1 week.

The field-emission scanning electron microscope (FESEM) photomicrographs, in Fig. 1, indicate that extensive morphological changes occur to the SiO_x/Si and SiO_x surface microstructures after 30 min of organosilane treatment; no such morphological changes were seen on short time (up to tens of seconds) immersion. Because of the loss of porosity on prolonged treatment, all films showing evidence of morphological change were eliminated from this study, which then concentrated on films treated for less than 10 s.

Fig. 2 shows photoacoustic FTIR spectra of nanoporous SiO_x/Si and SiO_x thin films after
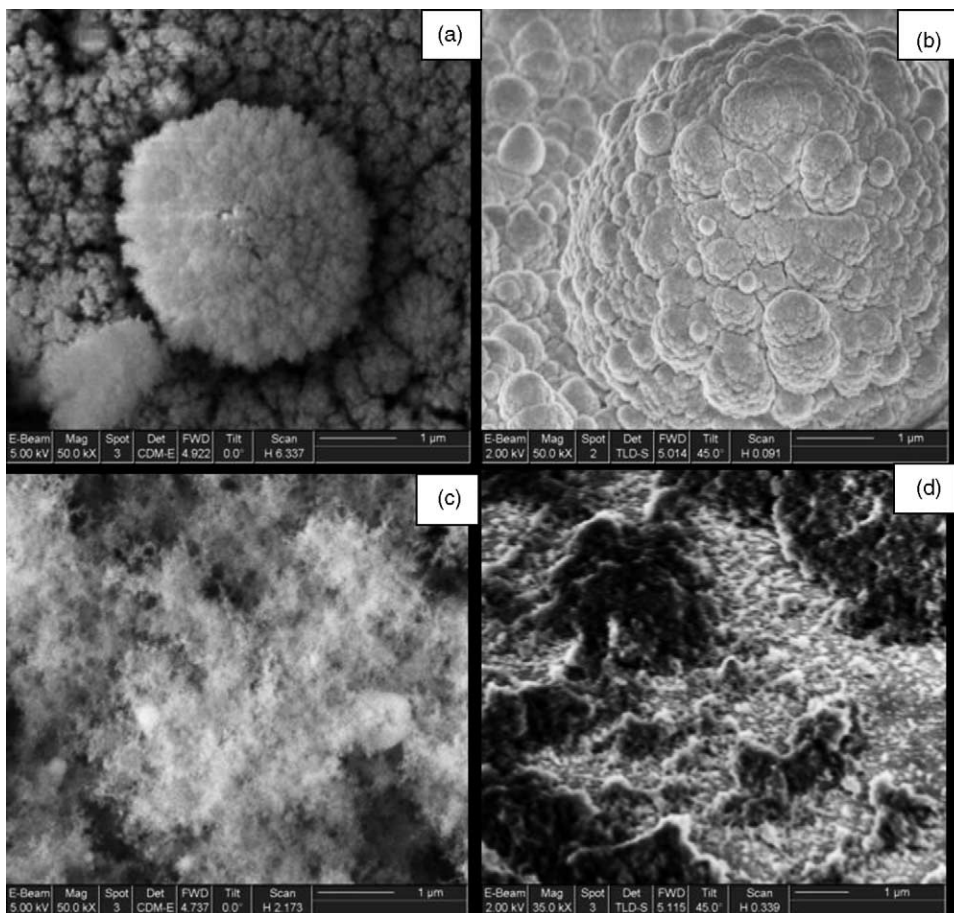
Fig. 1. FESEM photomicrographs of nanoporous SiO_x/Si (a) before and (b) after 30 min of organosilane treatment, and of nanoporous SiO_x (c) before and (d) after 30 min of organosilane treatment.

organosilane surface treatment. The spectra in Fig. 2 were not normalized since, on surface treatment, reaction [15] causes changes in all the peaks. For this reason, the same samples used for the *as-prepared* spectra were subsequently treated and immediately used for the *after treatment* spectra, and all were obtained under identical conditions.

New component peaks appear on treatment; among them are those at (i) 3366 and 3304 cm^{-1}, due to N–H stretching, as verified using the laser-deposited porous SiN_x film (not shown), (ii) a shoulder at $\sim$1250 cm^{-1}, due to Si–C stretching, and (iii) a broadening and shift of the Si–O–Si peak maximum toward lower wavenumbers, with a shoulder at 1063 cm^{-1} indicating the appearance or increase of a new peak due to Si–

O–Si stretching; all represent new bonds from the bound organosilane. As previously shown [16] and recently confirmed by us [17], photoacoustic signals from porous SiO_x surfaces are strongly enhanced by the expansion and contraction of both the pores and the gas within them, caused by the photoacoustic process. By comparison, nonporous SiO_x/Si and SiO_2 substrates (not shown) manifested almost undetectable signals on similar exposure to organosilane. The greater peak amplitudes, for SiO_x than for SiO_x/Si, imply a more porous SiO_x film.

The surface chemical compositions (several nm) of these nanoporous films were determined by XPS, an example of which is seen in Fig. 3 for SiO_x/Si. The presence of a N1s spectrum for the modified surface
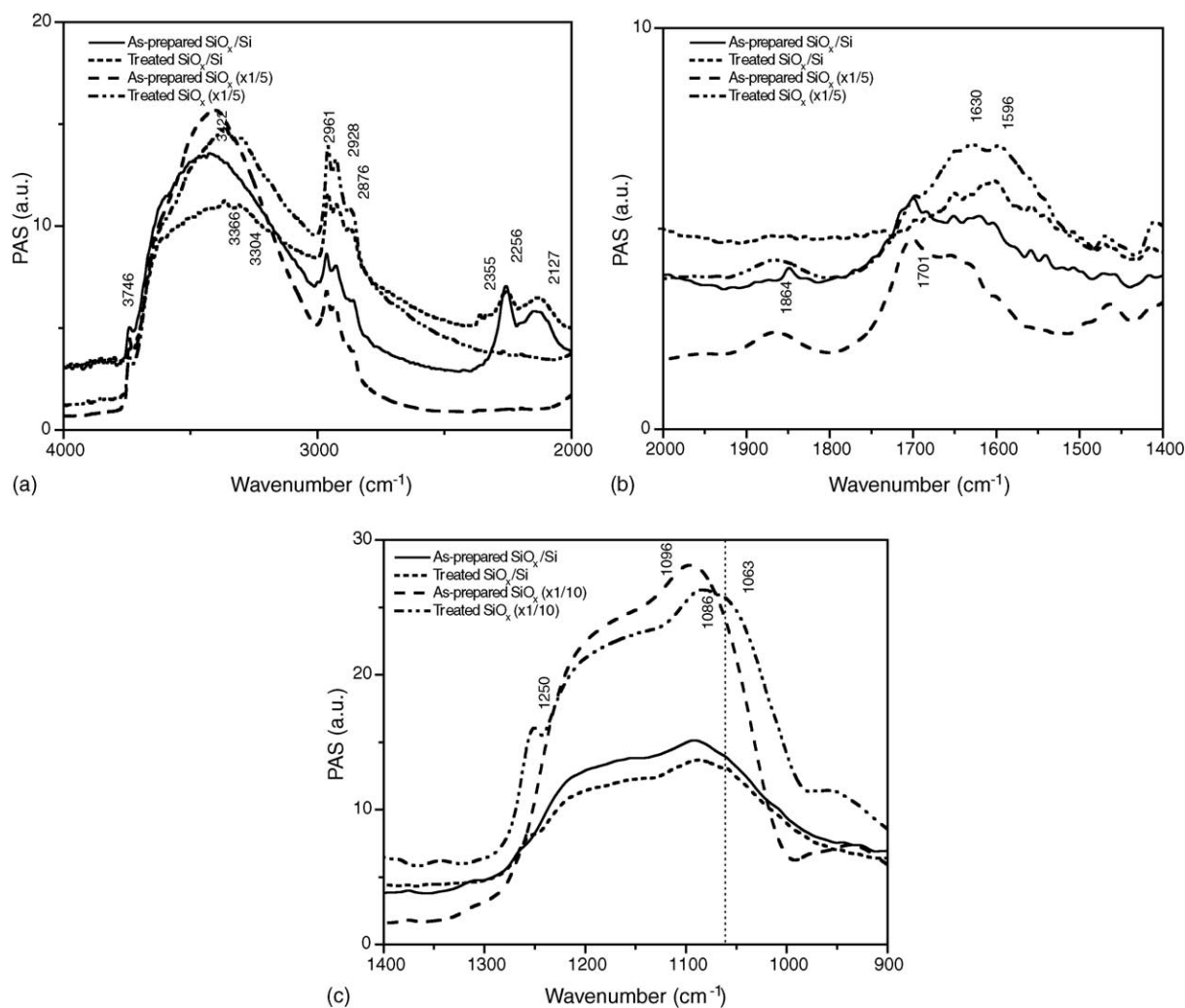
Fig. 2. Photoacoustic FTIR of nanoporous SiO_x/Si and SiO_x before and after organosilane treatment: (a) 2000–4000 cm^{-1}, (b) 1300–2000 cm^{-1} and (c) 600–1400 cm^{-1}.

(Fig. 3 and insert) clearly indicates that the organosilane has been grafted onto the surface. N exists in two forms: the peak positions (NIST XPS Data Base, http://srdata.nist.gov/xps/main_search_-menu.htm) suggest these forms to be amine (399.7 eV) and ammonium ion (401.8 eV). This is confirmed by the presence of photoacoustic FTIR stretching and deformation peaks for N–H ($\sim$3366 and $\sim$1664 cm^{-1}) and for N^+–H ($\sim$3304 and $\sim$1596 cm^{-1}). The O1s spectrum (not shown) is symmetric and narrow, with a FWHM of $\sim$1.8 eV, characteristic of a single O environment, as one would

expect for a situation in which all the oxygen-containing bonds are of the form Si–O–Si. There is also little change in the Si2p spectrum, before and after treatment (not shown), indicating that the maximum thickness of one organosilane monolayer contributes little to the overall Si2p spectrum.

Thus, both photoacoustic FTIR and XPS have confirmed the surface modifications of SiO_x/Si and SiO_x by short-term treatment with aqueous γ-aminopropyl dimethyl ethoxysilane, H_3N–$(CH_2)_3$–$Si(CH_3)_2$–OC_2H_5. Despite the fact that no more than one monolayer of organosilane was deposited, the
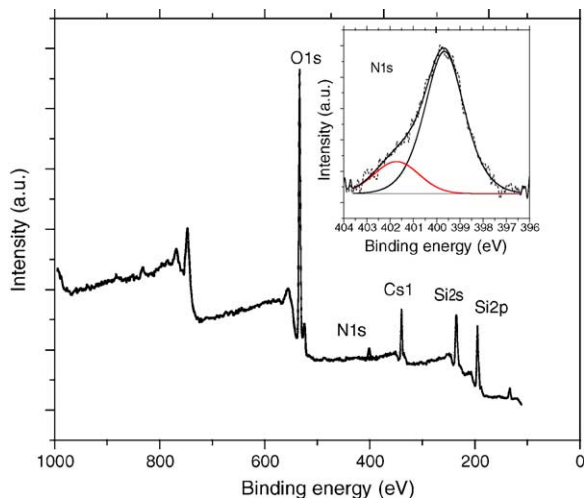
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Fig. 3. A survey spectrum of nanoporous SiO_x/Si after organosilane treatment; the insert is the high resolution N1s spectrum.

FTIR peaks manifested by the modification are strong and clearly visible. This visibility is due to the signal enhancement caused by the expansion and contraction of both the pores and the gas within them [16,17], during the photoacoustic process. This, coupled with the potential for further bonding of the functionalized organosilane with biomolecules, makes oxidized nanoporous Si a prime candidate for use as an IR biosensor.

In summary, we have demonstrated that mono-functional organosilanes can react with Si–OH groups on the surfaces of nanoporous SiO_x/Si and SiO_x substrates. The functionalized surface can be used to immobilize biomolecules, whose presence is revealed with a higher sensitivity than on nonporous surfaces.

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