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Integrating Ormosil films onto microstructured semiconductor substrates

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Abstract

A process of heterogeneously integrating organically modified siliceous aerogel (Ormosil) films onto microstructured substrates is presented. These substrates are architecturally designed to mimic photon detectors for remote sensing applications. Here, ultrasonically homogenized Ormosil sols are drop-cast onto silicon micropyramidal arrays then dried in the ambient to produce highly porous low-density siliceous films with excellent uniformity. The highly facile process yields films endowed with high optical transmittance, high static contact angle of 168°, excellent thermal stability up to 400 °C and, to some extent, excellent adhesion to the microstructured substrates on which they sit. Additional planarization benefits are easily afforded by controlling the substrate arraignment during the ambient drying process which the sol undergoes. In contrast, only conformal films were obtained when sols were spin coated over similar microstructured substrates. In correlating the resultant macroporous films' structural integrity with the underlying substrate topography, this study established that the weak physical bond between the facets of the microstructures and gel acts as crack nucleation points that induce and exacerbate crack propagation within the film. This phenomenon does not manifest itself when thinner films are prepared even on the same microstructured substrates as well as films of similar thickness on planar substrates. Initial studies establish that the non-homogenized sols can yield macroscopic aerogel monoliths with properties akin to those exhibited by supercritically dried monoliths. It is our belief that this study can enlighten the intricacies and pitfalls encountered when fabricating macroscopically monolithic Ormosil films over topographically structured surfaces.

Keywords: Ormosils; Planarization; Drop-casting; Thin films; Superhydrophobic

1. Introduction

Semiconductor microstructures of varied configurations, e.g. low-aspect-ratio micropyramidal arrays, are architectures of choice for a number of specialized applications, such as advanced sensors, capable of detecting a wide spectrum of photons over varied distances [1]; these have a multitude of applications that include medical diagnostics, analytical applications [2], artificial vision for remote sensors [3,4] and enhanced vision for everyday driving [5,6]. Some of these applications require sensors to be exposed to the ambient for efficient photon collection [2]. While this immensely enhances their sensitivity, their survival is then at the mercy of their particulate-laden surroundings, which are often deleterious to the arrays' mechanically fragile architecture. In order to extend their lifetime, the need to protect them with secondary coatings is pertinent [7].

Spin-coated poly(styrene), poly(methyl methacrylate) and poly(ethylene oxide) films on top of target surfaces have been extensively used as protective layers due to their

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ability to tolerate the additional thermal, chemical and mechanical processes required to render devices topographically planar [8–13]. Others have targeted polyimides as alternatives to high-temperature intolerant and mechanically inferior polymers [14,15]. Cross-linked forms of bisbenzocyclobutane have been used for these purposes especially for the planarization of group III–IV microstructures. In addition to polymers, siliceous films derived from spin-on-glass have been explored, due to their excellent thermal compliancy and mechanical properties [16]. Although the above-described optically clear materials provide excellent structural protection, they are not impervious to other irradiations outside the visible range. In addition, they possess high refractive indices that could potentially act as interference barriers to incoming irradiation, thereby reducing the sensitivity of the detectors. As an alternative, poly(tetrafluroethylene) (Teflon AF), with its low refraction index, high thermal resistance, high chemical inertness and high transparency over a wide optical window has also been used [17–19].

Nonetheless, highly sensitive irradiation sensors geared towards remote sensing applications would require planarization materials with indices as close to that of air as possible. To that end, siliceous aerogels offer the best choice given that their refractive indices can be as low as 1.02 [20]. Further, the antireflective capabilities afforded by their ultra-low density protects the incoming irradiation from interference, thereby maximizing its chance of hitting the detector. In addition, their inherent nano- and microsized pores accord them tremendous superhydrophobicity and render them impermeable to moisture. Recent reports have highlighted their self-cleaning capabilities, akin to those of the lotus leaf [21]. This is especially important since any condensate atop the detectors or on the protective film thereof would significantly increase the refractive index of the medium, thereby interfering with the incoming irradiation. Additionally, new synthetic protocols for these highly porous materials and their subsequent modification with organic moieties [22] can reduce their inhomogeneity, thereby curtailing their tendency to scatter light. Moreover, these films can be inexpensively processed under ambient conditions [23,24]. They can be readily affixed on to desired substrates via dip and spin coating techniques [21,23]. Consequently, they have been incorporated into both active and passive devices as antireflective coatings [25,26], thermal isolation layers for uncooled thin-film imaging devices [27] and as inter-metal dielectrics for high-performance ultra-large-scale integration devices [28,29].

While these reports have demonstrated the applications of aerogel films on a variety of topographically planar substrates [30], to the best our knowledge methods of integrating these films with microstructured surfaces such as micropyramidal arrays geared towards remote photon detections have not been reported [1]. This is especially important given that the topographical morphology of a surface directly influences fluid mass migration during deposition, especially if dip- and spin-coating techniques are used [31]. Thus, if spin coating were to be employed to deposit Ormosil films, the resultant film would likely exhibit a conformal morphology [10,32]. Unlike polymers, Ormosil films cannot be rendered topologically planar using mechanical and thermal processes due to their intrinsic porosity, complex cross-linked matrix and low density. A need to develop alternatives to spin and dip coating methods for depositing morphologically planar aerogel films on to microstructured surfaces therefore exists.

In this paper we report such an endeavor using a drop-casting platform. We use dummy substrates to validate and develop a process that will eventually be used for integrating aerogel films onto actual photodetectors with similar topographical microstructures. Our approach is inexpensive, very simple and produces films of unrivalled planarity over very large areas. Previous endeavors by other researchers have shown that topographically monolithic Ormosil films can be deposited on to planar substrates [23,33,34]. While this is true based on reported atomic force microscopy and scanning electron microscopy (SEM) micrographs, such films have not been demonstrated on microstructured substrates. We show that Ormosil films on microstructured substrates unlike those arraigned on planar substrates are prone to cracking. We compare the physical, thermal and optical properties of monoliths, thick and thin films prepared from two Ormosil sols containing slightly different proportions of silicon dioxide and its methylated counterpart. Compared to their spin-coated counterparts, drop-cast films are characterized by improved morphology, consistent topology and are devoid of the "coffee ring" effects that are endemic in the former [35,36].

2. Experimental

2.1. Materials and instrumentation

Tetraethyl-orthosilicate (TEOS), methyltrimethoxysilane (MTMS) and methanol (MEOH) were purchased from Sigma Aldrich. Oxalic acid and ammonium hydroxide (25%) were purchased from Fluka. Ethanol, hydrochloric acid (37%) (HCl) and sodium hydroxide (NaOH) was purchased from Alfa Aesar. Unless stated otherwise, all other chemicals were purchased from WRS and used as received. Optical studies were carried out on an Ocean Optics Spectrometer. Fourier transform infrared spectroscopy (FTIR) studies were carried out on a Niclolet Magna 560 FTIR spectrometer. Film images were taken on a Hitachi S-4100 field emission scanning electron microscope and a JEOL FEI XL30 scanning electron microscope. Surface profiles were extracted and processed from SEM micrographs using Gwyddion.

2.2. Substrate preparation

Glass substrates used were immersed in piranha solution for 3 h, and then rinsed in water followed by alcohol. They were subsequently dried under a nitrogen spray. Silicon