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Low temperature N_2-based passivation technique for porous silicon thin films

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ABSTRACT

A technique is presented for the passivation of porous silicon (PS) thin films via nitrogen based annealing at the lowest temperature ever reported. Annealing freshly anodized PS thin films at temperatures as low as 520 °C under N_2 flow in a rapid thermal annealer produces films that show no change in refractive index when exposed to ambient conditions over 60 days. These films also exhibited chemical resistance by surviving a brief dip in both concentrated KOH and buffered HF. Unlike most other PS surface passivation methods, this technique causes negligible reduction in refractive index of the annealed PS thin films. Passivation only occurs when dangling bonds and mono-hydrides populate the PS surface, providing a path for thermal interactions with the N_2 gas.

1. Introduction

Porous silicon (PS) has proven to be an excellent candidate for fabricating optical thin film-based devices, due to its rapid, simple and low cost fabrication. Multilayers and single films of PS have been utilized in a variety of fields including opto-electronics [1], chemical sensing [2] and biomedicine [3]. However, the very large reactive surface area of PS films, primarily consisting of mono-hydride and di-hydride terminated silicon atoms [4], results in as-anodized PS surfaces being highly unstable. The hydride terminated PS surface is a poor barrier to oxygen diffusion in ambient conditions, causing the refractive index, mechanical and chemical nature of PS thin films to vary over time [5].

Previous studies to develop methods for achieving optical stability in PS thin films, include use of capping layers [6], thermal oxidation [7], thermal carbonization [8] and nitridation [9,10]. Capping of PS requires expensive and time consuming deposition techniques such as molecular beam epitaxy or chemical vapor deposition, negating the aforementioned benefits of using PS thin films. Though simpler, thermal oxidation and carbonization lower the as-fabricated PS refractive index, reducing the index contrast and hence bandwidth of optical devices that can be fabricated [11]. Carbonization through the immersion of PS and pre-oxidized PS [12,13] in hot aqueous organics, developed by Koshida and co-workers, results in an increase in the refractive index of the thin film, and is highly stable, yet takes a number of months to achieve stability [13]. Nitridation has the potential to stabilize the optical properties while having minimal effect on the refractive index, and is a relatively simple and inexpensive technique to implement. However, to date, nitridation has proven challenging to achieve without detrimental effects, due to high annealing temperatures used [9,10], which causes significant deformation of PS thin films [14,15].

This paper presents an initial study on the effect of annealing in a nitrogen atmosphere at reduced temperatures, including successful passivation at the lowest temperature ever reported for the passivation of PS thin films via nitrogen based annealing. Previous studies on the thermal nitridation of PS and bulk silicon have annealed the samples at temperatures greater than 1000 °C in atmospheres of either NH_3 or N_2 [9,10]. Annealing at temperatures in excess of 700 °C causes extensive sintering of the PS skeleton, inducing interface roughness and pore conglomeration, resulting in

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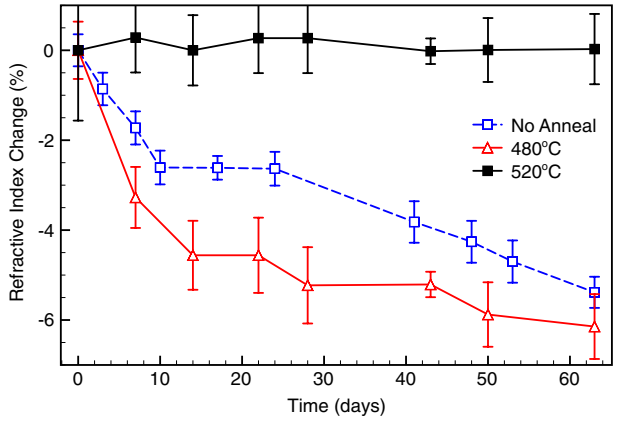

Fig. 1. Variation in refractive index over time from the as-annealed values, for the annealed samples, and as-fabricated value for the non-annealed sample.

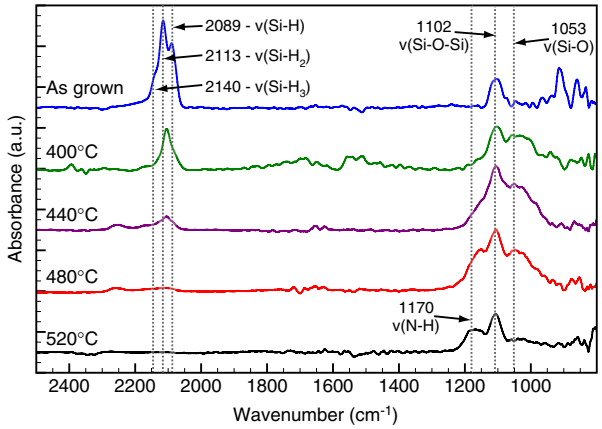

Fig. 2. FTIR spectra of samples annealed in nitrogen atmosphere at various temperatures.

an undesirable change in the optical properties of the films [14,15]. Hence, determining the minimum temperature required to passivate PS is critical to achieving stable PS thin films with desirable optical properties for use in multilayer devices.

2. Experimental

The samples used in this study were fabricated from Cz-grown, (100) oriented, p-type crystalline silicon with resistivity of ∼0.09 Ω cm. Anodization was carried out using a single tank electrochemical cell (the specific design is discussed elsewhere [16]), with an ethanoic HF solution for the electrolyte (3:3:14 of HF:H_2O:C_2H_5OH). All samples presented were anodized with a current density of 10 mA/cm^2 for 120 s to produce thin films with nominal thickness and refractive index of 772 nm ± 6 nm and 1.47 ± 0.01 respectively. All values for refractive index and extinction coefficient presented are obtained at a wavelength of 750 nm. Physical thickness measurements were performed with a Zeiss 1555 Variable Pressure Scanning Electron Microscope (VPSEM). Refractive index and extinction coefficient were extracted by fitting a characteristic matrix model to measured reflectance spectra [11], where the error bars presented are related to the goodness of the fit for extracted values. The error bars associated with thickness measurements are the standard deviation of multiple measurements on the given sample.

Annealing was carried out in an Anneal-Sys ONE rapid thermal annealer (RTA) at temperatures of 400, 440, 480, 520, 560, 580, 600, 800, 900 and 1000 °C, with a temperature ramp rate of 20 °C/s and a N_2 flow rate of 1000 sccm. The time taken between completion of anodization and commencement of annealing was within the range of 15–40 min. Before annealing, the samples were sealed in the RTA chamber, which was evacuated to 10^{-6} Torr and purged with N_2 three times to remove any residual oxygen or water, which are known to greatly affect nitridation experiments [17].

3. Results and discussion

Fig. 1 presents the strong contrast in optical stability between PS samples annealed at 480 °C and 520 °C. All samples annealed at temperatures 520 °C and greater displayed similar high optical stability to that shown by the 520 °C sample in Fig. 1. Optical stability in PS thin films has not been observed at such low annealing temperatures for either oxygen- or nitrogen-based previously reported methods. The temperature at which optical stability is observed coincides with the complete desorption of hydrogen from the PS surface, typically occurring at temperatures greater than 475 °C [4].

The FTIR spectra of the samples annealed between 400 °C and 520 °C, and of a non-annealed sample, are presented in Fig. 2. The spectra were obtained with a PerkinElmer Spectrum-One FTIR spectrometer. As will be detailed below, comparing the FTIR spectra of the various samples reveals a decrease in the presence of Si–H bond configurations and the appearance of a possible N–H bond as the annealing temperature is increased. Note that a Si–O–Si resonance is observed at 1102 cm^{-1} for all samples, corresponding to the well known residual oxygen impurities in Cz grown silicon wafers [18].

The FTIR spectrum of the non-annealed sample illustrates the typical hydride terminated PS surface, where a range of Si–H_x bond configurations are observed at wavenumbers between 2089 and 2140 cm^{-1}. These signals subsequently reduce as the annealing temperature is raised, corresponding to hydrogen desorption. Hydrogen desorbs from PS surfaces in a multistep process, where firstly the Si–H_2 and Si–H_3 desorbs to form H_2 and Si–H at temperatures between 350 and 475 °C, and as the temperature is increased further the Si–H desorbs to form H_2 and silicon dangling bonds [4]. This is evidenced by the complete disappearance of the Si– H_x bond configuration signals in Fig. 2 for samples annealed at 480 °C and above. Further, the onset of complete Si–H desorption at 475 °C corresponds with the observation of a possible N–H resonance at 1170 cm^{-1} in samples annealed at temperatures ≥480 °C [19]. Due to the doping levels of the silicon substrate, free carrier absorption prohibits the observation of Si–N stretching modes at ∼900 cm^{-1}.

Finally, an additional Si–O resonance at 1053 cm^{-1} is observed in samples annealed at 480 °C or lower. However, the sample annealed at 520 °C does not exhibit this resonance, further indication that surface passivation is only completed in samples annealed at temperatures higher than 480 °C. The strong N–H resonance observed at 520 °C would suggest that dangling bonds, hydrogen and a minimum temperature is required for successful passivation of PS surfaces.

Fig. 3 shows the (a) physical thickness, (b) refractive index and (c) extinction coefficient of the PS thin films for the unannealed sample and as a function of annealing temperature. The most striking feature of Fig. 3 is the abrupt reduction in physical thickness (Fig. 3(a)) for samples annealed between 400 and 480 °C. The distinct reduction in PS thickness can be observed from the SEM cross-sections presented in Fig. 4. Comparison of the SEM cross-sections of two PS samples cleaved from the same PS thin film and annealed at 400 °C and 800 °C, respectively, reveals an 87 nm difference in thickness. Importantly the porous structure is maintained uniformity over the whole layer thickness. This reduction in thickness of 11% again correlates well with the temperatures required for hydrogen desorption from PS top