Formation of densely populated SiO_x microtree-like structures on the Si (100) surface, using excimer laser irradiation in air

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ABSTRACT

SiO_x microforest-like structures have been produced on Si (100) surfaces by pulsed excimer laser irradiation in air. Scanning electron microscopic observations have indicated these structures, which are composed of aggregated nanoparticles, to be 1-5 μm in diameter and 10-20 μm high, and to have the appearance of trees. XPS analysis has shown them to be composed of a-SiO_x ($1<x<2$). They show strong photoluminescence at 680 nm. Compared with previously published data on Si microcolumns, microspikes and micro-tipped structures, produced using pulsed laser irradiation, our microforest-like trees have many sharp nanoscale branches, which may require lower emission voltages in application such as field-emission sources in plasma displays.

Keywords: Surface microstructure modification, nanostructures, laser ablation, silicon, surface analysis, photoluminescence

I. INTRODUCTION

Recently, the study of the formation of Si microcolumnar arrays through the use of femtosecond or nanosecond laser irradiation near the melting temperature [1-4] has attracted considerable attention. These microcolumn arrays can be grown on Si surfaces in air, or in SF_6 or Cl_2 gas environments. Most microcolumns are sharp, conical spikes. Their axial direction is aligned along the incident laser beam, with high aspect ratios. It is thought that such microcolumns may have interesting potential application; as an example, field-emission sources for plasma displays, using significantly lower emission voltage has been found [5], although the tips should, in future, be sharpened to a greater extent, in order to produce nanoscale features necessary to increase the geometrical field-enhancement factor and reduce the emission threshold field [6]. They may also be used as microarray-type photoluminescence devices[7]. Wu et al.[8] showed that a quasi-ordered array of sharp, conical microstructures, up to 50 μm high and about 0.8 μm wide near the tip, may be produced by femtosecond laser radiation in SF_6 (laser-induced chemical etching). It is interesting to note that Si microcolumns may have as high as 90% absorption from the near ultraviolet (0.25 μm) to the near infrared, and may be enhanced by high density impurities, structural defects in the silicon lattice, and surface texturing. The authors believe that such properties might make possible silicon-based detectors for infrared radiation.

Recently, Georgiev et al.[9] found they could produce very sharp conical tips, with heights of 1 μm and apical radii of curvature of several tens of nanometers, by excimer laser radiation of Si crystalline thin films (200 nm thick) deposited on silica substrates, using a 50 μm diameter pinhole mask. The patterns with sharp tip arrays may be applicable for low voltage field emission device fabrication. Experimental results indicated that the microcolumnar patterns could not only be affected by laser radiation conditions, but also changed by variations in the mask[10].

Although now the mechanism of laser-induced periodic surface structures (LIPSS[11]) is better understood, the origin of microcolumns has not been clarified. Sánchez et al.[12] proposed a hydrodynamic growth mechanism, and Pedraza et al.[3] proposed a mechanism that is similar to the vapor-liquid-solid process with a combination of pulsed laser melting of the tips of the columns and the deposition of Si from the intense flux of vapor produced by the ablation of the surface regions between columns. The study concluded that the formation of the microcolumns is strongly dependent on the gas

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environment, being enhanced in air or other oxygen-containing ambients. A better understanding of the processes involved would help in the fabrication of well-defined microcolumns and Si-related surface structures.

Here, we report our preliminary results on the formation of nanostructured Si micro-trees produced at lower fluences of excimer laser radiation in air. Their photoluminescence (PL), surface morphology (SEM), and chemical structure (XPS) have been characterized.

II. EXPERIMENTAL

Si surface microstructural modifications were performed by pulsed KrF (248 nm, 20 ns FWHM pulse duration) excimer laser radiation with the number of pulses ranging from 300 to 1000. The irradiated area varied with the laser fluence but was typically 2×5 mm^2. Commercial n-type (100) Si wafers were irradiated at pulse repetition rates of 30 Hz in air, with the beam perpendicular to the Si wafer surface.

XPS was carried out in a VG ESCALab Mark II with non-monochromated Mg K_α radiation (1253.6 eV). Peaks were calibrated to the C1s contaminant peak (285.0 eV) for all core levels. The VG Avantage software was used for spectral deconvolution and peak area integration. Photoluminescence measurements were carried out on a LSM 510 META confocal Raman microspectroscope, using an Ar^+ laser at 488 nm as the excitation source (20 mW), and a GaAs photomultiplier as the detector.

Photoacoustic Fourier Transform Infrared Spectroscopy (PA FTIR) was carried out using a He-purged MTEC 300 photoacoustic cell in a Bio-Rad FTS 6000 spectrometer, at the spectral resolution of 4 cm^{-1}. The 5 kHz modulation frequency used probed the entire sample thickness.

III. RESULTS

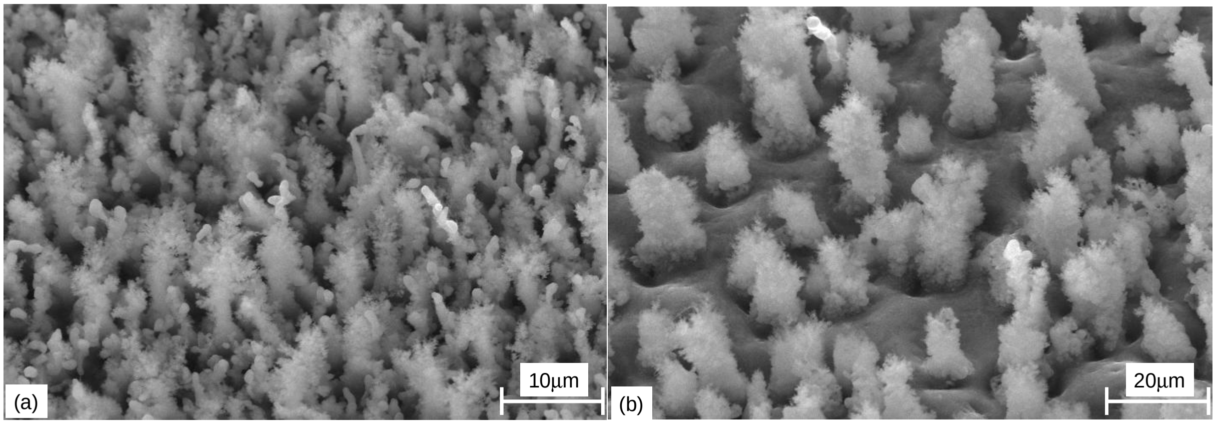


Figure 1 SEM micrograph after laser irradiation of Si (100) in air under fluences of (a) 1.5 J/cm^2, and (b) 1.1 J/cm^2

Laser irradiation produces strong plumes in the radiation region in air, and causes a dark gray surface coloration. Figure 1 shows scanning electron photomicrographs of surface microstructures after ~ 500 pulses, at fluences of about (a) 1.5 and (b) 1.1 J/cm^2. Micrometer scale tree-like structures are formed on hillocks on the Si surface. These microtrees are always well aligned with the laser incidence direction. With increased radiation fluence, higher tree densities are formed. The heights of these trees can be as much as 5-10 μm, with diameters of about 2~5 μm. The micro-trees are composed of nanoscale particles, and have high porosities. Several of the microtrees appear to be joined by a denser material that appears to be similar to what was found by others[1-6]. Our initial observations also indicate that tree nucleation is inhomogeneous, and invariably takes place at the sides of deep grooves or pits. New microtrees-like structures continue to be nucleated as the number of pulses increases. The nucleation of new microtrees continues to take place until a dense "forest" has been formed. All these processing are similar to the case of the laser-induced formation of microcolumns at the Si surface[13]. We did not observe such microtrees in vacuum or in a He environment under same laser fluence. The laser radiation power density at the Si surface plays an important role, with higher energy densities forming microcolumnar patterns

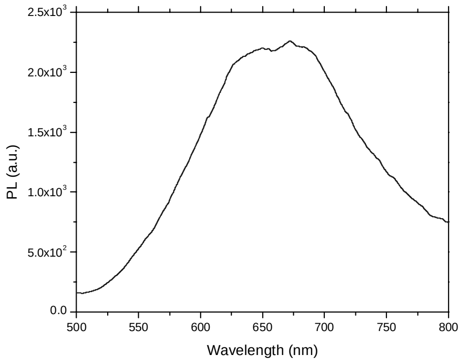


Figure 2 Photoluminescence of nanostructured Si microtrees

Photoluminescence measurement are shown in Fig. 2. A broad peak is observed at about 650 nm (~1.85 eV). A similar PL peak shape has been observed in microcolumnar SiO_x structures and chemical etched porous Si[14], Si nanostructured thin films[15], SiO_x/Si layers produced by CO_2 laser optical breakdown processing[16,17] and similar structures[7,18,19].

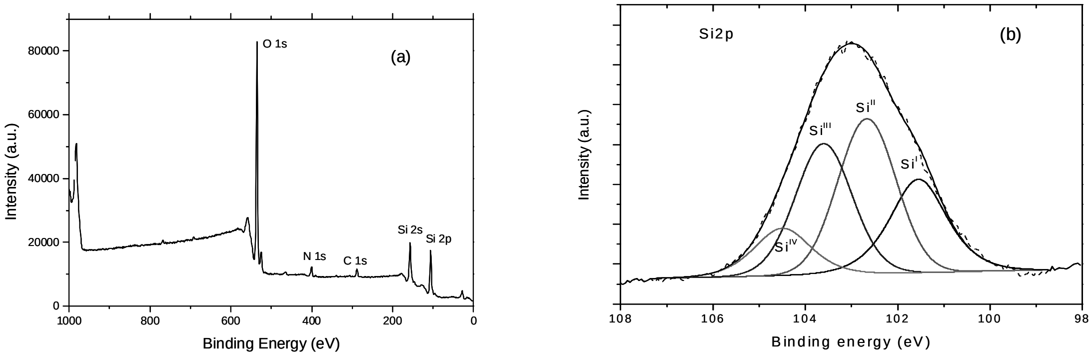
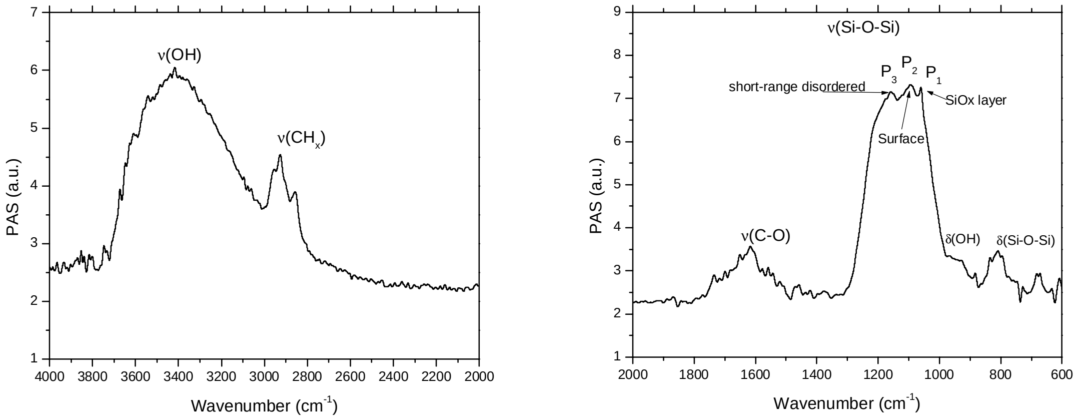


Figure 3 XPS spectra of nanostructured Si microtrees (a) survey scan, (b) Si2p and its deconvolution

An XPS survey spectrum of the treated Si surface (Fig. 3a) shows that the main component is SiO_x, with C- and N-containing contaminants. The total concentration of C and N is determined to be less than 4 at %. The very broad Si2p spectrum is composed of several chemical components. Based on our previous analytical work, we separated the spectrum into its components, as shown in Fig. 3b. Clearly, Si^0 is absent, indicating the absence of a Si core within the XPS Si detection depth (around 10 nm) and sensitivity. The estimated x value in SiO_x is about 1.4-1.6.



(a) (b)

Figure 4 Photoacoustic FTIR spectrum of nanostructured Si microtrees

PA FTIR provides greater depth information on the thin films. As we showed previously[20], PA FTIR signals are greatly enhanced in porous SiO$_x$, due to the expansion and contraction of both the pores of the solid and interstitial gas within them. Typical PA FTIR spectra are shown in Fig. 4. Hydroxyl stretching is observed at 3400 cm^{-1} (Fig.4 a), with CH$_x$ contaminant stretching at 2800-3000 cm^{-1}; weaker CO and COOH stretching appear 1600-1750cm^{-1}. Strong Si-O asymmetric stretching appears at 1000-1300 cm^{-1}. The band can be decomposed into three components: that at 1045 cm^{-1} is attributed to Si-O-Si bridge structure, that at 1085 cm^{-1} is attributed to non-bridged Si-O-Si at the free surface, and that at 1165 cm^{-1} is attributed to the asymmetric stretching (AS) of Si-O-Si associated with short-range, disorder-induced, LO enhancement[20]. The significant enhancement of the surface nonbridging Si-O structure may be responsible for the higher porosity of the Si microtree composed of nanoscale particles. For example, relative intensity ratio of peak P$_2$ and P$_3$ are close one, compared to 0.2 (P$_3$/P$_1$) and 0.6 (P$_2$/P$_1$) in amorphous SiO$_2$[20], suggesting that there is greater amount of short-range disordered SiO$_x$ structures in the nanostructured microtrees

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IV. DISCUSSION

We believe that microtrees form on the redeposition of Si from the laser ablation. Although the profiles of the microtrees are similar to microcolumns produced by laser irradiation, it is difficult to image the construction of microtrees from nanoparticles by the VLS (vapor-liquid-solid) process[3]. From our results, we proposed the following formation mechanism, based on the fact that the fluence used is higher than the ablation threshold (1.0 J/cm^2). Initially, laser radiation leads to the ablation of Si atoms and/or clusters, followed by the growth of the cluster and oxidation in air. Collisions with air molecules causes a reduction in kinetic energy, with a resultant clustering. The SiO$_x$ clusters are redeposited onto the molten Si surface, forming the tree-like structures found. Such SiO$_x$ trees has higher melting temperatures than the Si wafer and are nucleation sites for further redeposition during the subsequent pulses. Because of this, the laser power density and environments are two important factors contributing to the nanostructured SiO$_x$ microtree structures. Preferential nucleation from evaporated Si clusters plays an important role. This is because the SiO$_x$ clusters in the plume, with large amount of dangling bonds react with other clusters contacted during formation and redeposition. The high density of SiO$_x$ clusters in ablation region and preferential redeposition may lead to a very high growth rate of the microtrees (~50nm/pulse), similar to that of the microcolumn during laser ablation.

The photoluminescence of nanostructured Si thin films and porous Si layers is generally attributed to (1) quantum confinement effects[21], which assumes the PL to be due to electron-hole recombination across the fundamental nanostructure band-gap, and (2) oxide-related defects[22]. In addition, surface electronic states[23], assumed to act as traps that capture the electrons or holes, facilitating their recombination, are also thought to play an important role in visible PL emission. In microtree-like nanostructured SiO_x layers, XPS indicates that no Si is present at the core, suggesting that the quantum confinement model does not fit our case. It has been shown that SiO_x defects produced on extensive oxidation are related to the PL peak at 2.3 eV (or 540 nm)[24], and this has recently been confirmed by us[25]. Thus, it appears that the PL comes from local surface states of SiO_x having a high defect density and short-range disordered non-bridging Si-O-Si centers. The position of the PL may vary from 1.5 eV to 2.0 eV[24, 25]. Therefore, the PL of our microtree-like nanostructures appears to arise principally from SiO_x surface states, while the PL produced by the SiO_x defects gives a minor contribution near 540 nm.

CONCLUSIONS

Nanostructured Si-based microtree patterns have been produced by excimer laser radiation in air, at low power densities. The microtree patterns are a few micrometers in diameter and as high as 10 micrometers, with separations of several micrometers. The microtrees are composed of nanoparticles from the redeposition of SiO_x clusters ablated in air. The nanostructured SiO_x trees demonstrate strong visible photoluminescence, indicating potential applications in low voltage field emission devices.

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