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Ultrafast-laser-assisted chemical restructuring of silicon and germanium surfaces

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Abstract

This article reports a comparative study on texturing in silicon and germanium surfaces after exposure to femtosecond laser irradiation in the gaseous environments of sulfur hexafluoride (SF_6) and hydrogen chloride (HCl). The surface texturing results from the combined effect of laser-assisted chemical etching and laser ablation. Optimized processing conditions have produced features on the order of nanometers in size. We demonstrate for the first time that regular conical pillars can be formed in Ge and that HCl can be used to form regular conical pillars in Si.

Keywords: Femtosecond laser; Surface texturing; Ultrafast lasers; Chemical restructuring; Silicon and germanium surfaces

1. Introduction

Silicon and germanium are two of the most important electronic materials used in the semiconductor industry. Restructuring the surface of silicon has been an active area of research due to several reasons including: (1) it enhances the surface area and hence the effective active area of a device increases, (2) it can effectively trap more light for fabrication of high efficiency optoelectronic devices, (3) it increases catalytic actions due to large surface area, and (4) it can have possible biomedical applications.

Surface texturing by porosification of silicon has been extensively studied over decades and recently ultrafast laser-assisted surface texturing [1–8] has become progressively more popular due to several advantages: (1) unlike porous structures, regular sharp pillars can be formed in which the entire surface area is exposed as *exterior* surface, (2) the structural, optical and electronic properties can be well tailored by controlling the processing conditions, and (3) large area samples can be processed with automation. Nonetheless, the formation of regular conical pillars has only been demonstrated previously in silicon. Furthermore, while it is known unambiguously that the initial stages (i.e. during the first few laser shots) of surface texturing exhibit virtually no dependence on the presence and nature of the process gas, it is equally well known that the ultimate structures formed after hundreds of laser shots depend sensitively on the presence and nature (i.e. comparing vacuum to air to He to SF_6) of the process gas. The specific role of the chemical interactions that lead to structure formation are shrouded in mystery. In this study we report the laser texturing of silicon and germanium surfaces and compare their surface morphologies.

2. Experimental procedure

The Si(1 0 0) (B doped) and undoped Ge(1 0 0) wafers were cleaved into small chips and cleaned with acetone and methanol. Silicon and germanium chips were put successively on a stage inside a vacuum chamber (with base pressure ~1 mbar) mounted on a high precision computer controlled *X*–*Y* stage. The chamber was backfilled with 400 mbar SF_6 or HCl after rinsing several times with the process gas. The samples were then exposed to 1.4 mJ pulses of 800 nm/130 fs light at a repetition rate of 1 kHz from a regeneratively amplified Spectra Physics Ti-sapphire laser system. The laser beam was focused by a 1 m focal length coated lens and incident normal to the sample surface. The laser fluence was controlled by using a calcite Glan-laser polarizer.

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The spatial profile of the laser pulse was nearly Gaussian, though elongated in one axis compared to the other creating an elliptical profile, and the fluence was calculated using the spot size determined by exposing a small area on the sample surface to thousands of shots. In order to scan an area bigger than the laser spot size, the samples were translated using a motorized *X–Y* stage. Scanning also assists to make more uniform surface structures by smoothing out any shot-to-shot irregularities in the beam profile. By varying the scanning speed of the *X–Y* stage, the number of laser pulses impinging on the sample surface at a particular spot was controlled. The spot size was 0.3 mm along the minor axis and 0.6 mm along the major axis. Scanning was performed parallel to the minor axis. Samples were produced either with isolated single line scans or with large areas created by overlapping several line scans. The step size between scan lines was chosen to be sufficiently small (generally 0.38 mm) such that successive lines overlapped substantially, improving homogeneity. Homogeneity is further enhanced by performing two overlapping scans in orthogonal directions rather than one overlapping scan with an exposure of the same total number of shots. After laser processing, the samples were analyzed with a field emission scanning electron microscope (Zeiss SUPRA 40).

3. Results and discussion

Fig. 1. shows the SEM images of sharp conical pillars formed on the silicon surface produced with 240 shots of 130 fs laser pulses at a fluence of 0.6 J cm^{-2} in 400 mbar of SF_6 (Fig. 1a) and HCl (Fig. 1b), viewed 45° from the surface normal. The pillar size varies across the scanned laser line indicating the intensity variation of the laser fluence across the spatial profile of the laser pulse. We overlapped the scan lines to minimize height variation over a large area on the sample surface. The spikes that are obtained in SF_6 are ~ 15 μm tall and around 5 μm at the base.

On the other hand, under similar conditions, the structures formed in the presence of HCl are composed of taller pillars (~ 20 μm height) with a base dimension around 7 μm. It is evident from Fig. 1a and b that the pillars which are formed in SF_6 are narrower towards the tips compared to pillars formed in HCl. Although the pillar density is comparable in both cases, the pillars formed in HCl look stronger and relatively blunt towards the tip indicating that differences in the etch chemistry in the F/Si system relative to that of Cl/Si system are responsible for significant structural differences. The role of chemistry in structure formation is not well understood and it is not a trivial result that regular conical pillars are formed during fs irradiation in SF_6 as well as HCl. For example, regular conical pillars can be formed during ns irradiation of Si in the presence of SF_6 but they are not formed for ns irradiation in the presence of HCl [9]. During ns pulsed irradiation of Si, HCl produces significantly blunter tips, the pillars are much taller (>50 μm) and they are porous rather than solid core [9]. This is a further indication that the mechanisms of pillar formation are not the same for fs and ns irradiation. This result is also significant because chemical impurities, namely sulfur, incorporated during laser processing have been implicated in changing the optical and electronic properties of the textured surfaces [10]. By expanding the range of gases in which pillar formation is possible, we should be able to disentangle the effects on optical and electronic properties of geometric parameters from chemical parameters.

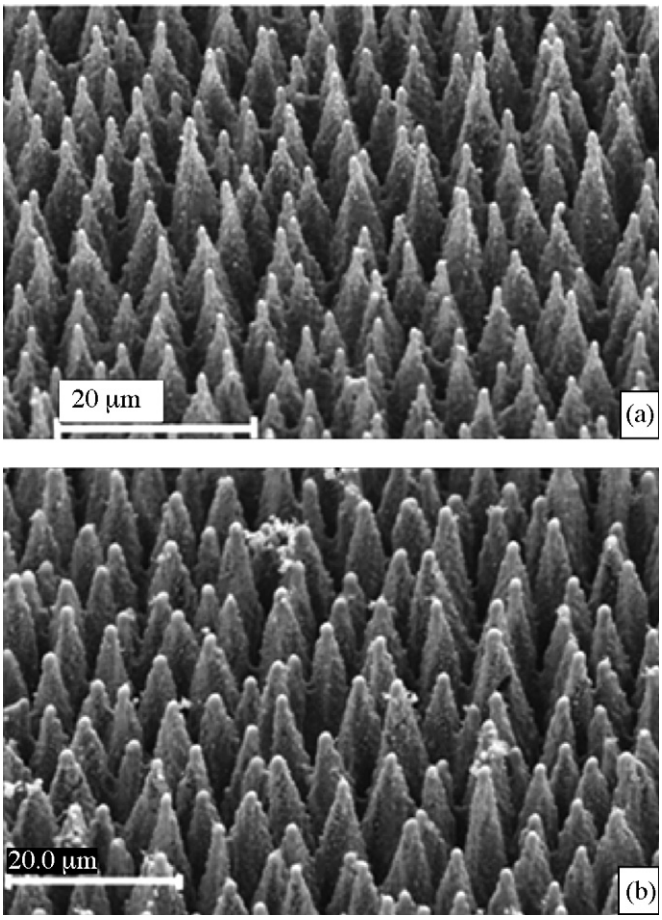

Fig. 1. SEM images of pillars, viewed 45° from the surface normal, formed in silicon surface by 240 laser pulses of 130 fs duration, 0.6 J cm^{-2} fluence in the gaseous environment of 400 mbar of (a) SF_6 and (b) HCl.

Fig. 2 displays SEM images taken for germanium samples treated under similar laser and gaseous conditions as in the case of silicon described above. A very different surface texturing was observed in germanium as is clear from Fig. 2. In the case of germanium processed in SF_6, we noticed two distinct features not observed under conditions that are similar to those used for silicon: (a) conical pillar formation with higher cone angle up to a neck and (b) atop these pillars very sharp spikes up to ~ 2 μm in length with ~ 100 nm tip radius. Nanoclusters formed during laser ablation are more abundant in germanium compared to silicon under similar laser conditions, which might be due to the lower melting temperature of the former. On the other hand, the germanium structures formed in the presence of HCl (Fig. 1b) are less densely populated, shorter, high cone angle, wider base, and exhibit greater variations in pillar height compared to silicon (Fig. 1a). It is interesting to note that gas phase silicon etching is anisotropic in HCl and the etch rate is ~ 20 μm min^{-1} for the Si(1 0 0) plane at temperatures in the