A Systematic Study of the Formation of Nano-Tips on Silicon Thin Films by Excimer Laser Irradiation

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ABSTRACT

Recently, we reported conditions for controllable, direct laser fabrication of sharp conical tips with heights of about one micrometer and apical radii of curvature of several tens of nanometers. An individual cone is formed when a single-crystal silicon film on an insulator substrate is irradiated in air environment with a single pulse from a KrF excimer laser, homogenized and shaped to a circular spot several microns in diameter. In this work, we present a study of the formation of such tips as a function of the laser fluence, the film thickness, and the diameter of the irradiated spot. Atomic force microscopy and scanning electron microscopy were used to study the topography of the structures. A simple mechanism of formation based on movement of melted material is proposed. We have also studied structures (nano-ridges) that resulted from irradiation with narrow lines (width of several microns) instead of circular spots.

INTRODUCTION

High-intensity pulsed laser radiation can be used to modify surfaces of materials and fabricate technologically desirable structures on a micrometer and sub-micrometer level. Besides their technological importance, such surface modifications can be of substantial scientific interest. The processes involved in such radiation/matter interactions are complex and usually non-equilibrium due to high heating and cooling rates, large temperature gradients and a variety of chemical and photochemical transformations. These processes and their interplay are often poorly understood, and therefore systematic studies of laser irradiation of materials as a function of a certain set of parameters are essential.

Recently \cite{1}, we reported conditions for controllable, direct laser fabrication of sharp conical nano-tips on silicon thin films and in this work we present additional results on this new technique. Reliable, simple and low-cost techniques for fabrication of micro- and nano-tips of silicon and other semiconductor and metal materials, as well as large, high-density arrays of such tips, are desirable in a number of technological applications. These include probes for scanning probe microscopy techniques, emitters for field-emission-based devices such as high-definition displays \cite{2,3} and other vacuum microelectronics applications \cite{4}. There is also a considerable amount of ongoing research on surface patterning of materials for biomedical applications \cite{5-7}, which could also benefit from new developments in the area of materials surface micro- and nano-structuring.

Laser fabrication techniques that utilize high-energy UV excimer lasers with large-area homogenized beam cross-sections can provide the advantages of high-resolution, high throughput, uniformity, highly localized heating, simplicity and reproducibility. In addition, combinations of laser techniques with other established technological steps could evolve into new, more flexible technologies. Remarkable Si columns with heights of about 20 \(\mu\)m and...
widths of 2-3 µm have been produced by multiple-pulse, large-spot, nano-second excimer laser irradiation (KrF laser, λ = 248nm) of Si wafers in oxygen and oxygen-containing ambient [8]. Conditions for nano-structuring of Si surfaces have been identified in a study of the irradiation of bulk Si as a function of the number and the fluence of the applied KrF excimer laser pulses in different gas environments [9]. In all of the above-mentioned cases, single-crystal Si has been subjected to multiple-pulse, large-laser-spot-area irradiation and there has been little or no control over resulting surface topography. KrF excimer laser irradiation by large-area scanning of amorphous Si thin films on Mo-coated glass substrates has been reported [10] to result in a sharp surface morphology that can be viewed as consisting of randomly situated, densely packed, nano-sized crystallites. The technique that we are developing allows us to controllably fabricate Si tips (and dense arrays of such tips) with heights in the range of 0.2 to 2 µm and apical radius of curvature of several tens of nanometers. In addition we will show first results on the fabrication of nano-ridge structures.

EXPERIMENTAL

Spatially homogenized, single pulses of radiation from a KrF excimer laser (λ = 248nm, Lambda Physik, model LPX 205) were used to image pinholes or slits onto uniformly illuminated circular spots or lines on the sample surface by means of a projection system with a demagnification factor of 8.9 and a resolution limit of 2 micrometers. The laser pulse energy was measured to be reproducible within 5%. Most of the work was done on commercially acquired silicon-on-insulator (SOI) wafers that consisted of 200nm (100) single-crystal Si bonded to a silica glass substrate. In addition, non-coated and Ni-coated SOI wafers that consisted of a single-crystal Si layer on 1 µm layer of silica on a bulk Si substrate (SOIS) were used. These were plasma-etch-thinned to different thicknesses of the Si layer in the range of 0.8 – 4.1 µm. The laser processing was performed in ambient, clean-room conditions, and the sample surface topography was then examined by contact-mode atomic force microscopy (AFM) on a Park Autoprobe LS AFM system using Contact Ultralever® tips. Some samples were coated with a thin layer of Au and then imaged by field-emission scanning electron microscopy (FESEM) on a JEOL JSM 6300F electron microscope at an accelerating voltage of 5KeV and a sample tilt of 60 deg relative to the electron beam.

RESULTS AND DISCUSSION

AFM images of a tips fabricated by single pulses at a fluence of 1.5J/cm² are shown in Fig.1. The z-scale of the images has been expanded by, approximately, a factor of 2 to better show the size and shape and of the tips and the changes in the surrounding irradiated area. We observe round and relatively flat circular depressions, the diameters of which roughly correspond to the size of the laser spot. This depression is, typically, several tens of nanometers below the original surface, and almost-conic tips appears in the center of the depressions. Pinhole masks with diameters 30, 40, and 50µm producing laser spots with diameters 3.4, 4.5, and 5.6µm were used to make the structures in Figures 1a, 1b, and 1c respectively. The apparent radius of curvature of the tip apex is about 50nm as estimated using the AFM scan. This apparent radius is in good agreement with the FESEM image of a tip fabricated with a 50µm mask and shown in Fig.2a. Because the samples were coated with gold prior to the FESEM work, the actual tip is likely to be even sharper than what we see in Fig.2a. Also, the Unilever® tips have a radius
Figure 1. AFM images of nano-tips fabricated with single 1.5J/cm$^2$ pulses and pinhole masks producing laser spots with diameters 3.4 (a), 4.5 (b) and 5.6µm(c).

of curvature of 10nm and cone half angle of 15°. Thus the 50nm radius of curvature in the AFM image, being a result of a convolution of the laser-formed cone shape and AFM tip shape, is also an overestimation.

We estimated the fluence thresholds for observable changes as a result of a single pulse irradiation (which we call simply “thresholds” from this point on) to be: 0.8J/cm$^2$ for the 50µm mask, 1.0J/cm$^2$ for the 40µm mask and 1.25 J/cm$^2$ for the 30µm mask. When pulses with considerably higher fluences (typically above 2.0J/cm$^2$) are used, a sub-micron hole through most of the Si film thickness develops in the center of the tip and the base of the tip widens. The formation of such sub-diffraction-limited (supper-resolution) ablation holes in SOI and other thin-film systems was also reported by us recently [11]. Fig.2 shows FESEM images of tips fabricated with a 50µm-diameter pinhole mask at a 1.5 (a) and 1.25 (b) J/cm$^2$. A reduction in the apical radius of curvature (estimated to be about 30nm the case of Fig2b), the diameter of the depression around the tip, and the height of the tip are clearly seen upon this decrease in the fluence. When larger pinhole mask (100µm diameter) were used, no tips formed – we obtained only ablation holes form above a threshold fluence of about 0.6 J/cm$^2$.

We attempted fabrication of nano-tips on SOIS samples with Si film thicknesses 0.8µm, 1.1µm, 2.3µm and 4.1µm. When using a 50µm pinhole projection mask, there were no observable changes on the surfaces of the films with thicknesses of 2.3 and 4.1µm after

Figure 2. FESEM images of (a) a tip fabricated by a single pulse with fluence of 1.5J/cm$^2$; (b) a tip fabricated by a single pulse with fluence of 1.25J/cm$^2$. 
single-pulse irradiation with fluences up to 3.0J/cm$^2$. In the 0.8μm and 1.1μm film thickness cases we measured thresholds of 1.5 and 1.75 J/cm$^2$ respectively. Fig. 3 shows AFM images of tips that were made on SOIS samples using a 50μm pinhole mask. The tip shown in Fig.3a was fabricated on a 0.8μm-Si film and the one in Fig.3b on a 1.1μm-Si film, both at a fluence of 2.0J/cm$^2$. These tips are also very sharp (about 30-50nm radius of curvature) with the one on the thinner film being taller – 0.7μm as compared to 0.6μm. Upon increasing the single-pulse fluence up to the highest achievable value (for our current set-up) of 3J/cm$^2$, we were still obtaining nice, sharp tips, with larger heights and without a crater or any considerable flattening on top. Fig.3c shows an AFM image of a nano-tip fabricated on a 1.1μm thick Si film with a fluence of 2.75 J/cm$^2$: the height of this tip (about 1.5μm) is considerably larger than that of the 2.0J/cm$^2$ tip.

Because of application-driven interest in fabricating magnetic nano-tips of the similar geometry and sizes, we also tried to find conditions for tips formation on SOIS films coated with a thin Ni film. The expectation was that if the same mechanism of formation of nano-tips were to work for this system, the Ni film would alloy with Si in a Si-rich but magnetic material which would comprise the tip. However, we were not able to obtain any structure that resembles even remotely the nano-tips described earlier. Above a threshold fluence (typically below 1J/cm$^2$), a single pulse irradiation by using a 50μm pinhole projection mask results in an ablation hole with a size defined by the optical spot image and a depth that increases with the fluence.

A complete analysis of the involved physical processes would be overwhelmingly difficult, if possible at all, and would need to account for [12]: temperature dependence of all material parameters; heat dissipation through radiation; evaporation and plasma formation just above the surface together with the corresponding laser radiation shielding; surface tension; overheating and overcooling; chemical transformations such as oxidation. Nevertheless, we believe that the brief, simplified, qualitative description, which we give next, identifies the dominant mechanisms and defines the important parameters that one would need in designing fabrication recipes.

The laser radiation is absorbed entirely in a thin surface layer of thickness that is less than 10nm thick (the absorption coefficient of Si at $\lambda$=248nm is about 2x10$^6$cm$^{-1}$). This surface layer becomes a source of heat that causes melting of the entire thickness of the film: under the conditions of irradiation, the depth of melting of bulk silicon would be more than the thickness of the film [13]. Because the underlying silica has much lower thermal conductivity than Si, heat is dissipated predominantly laterally through the surrounding Si film volume (especially once the entire film volume in the laser-irradiated spot is melted). The interplay of material properties of
the film and the substrate and the geometry (film thickness and irradiated spot size) is essential for the formation of the tips.

We have verified that irradiation of bulk Si wafers under conditions identical to those applied to the SOI samples (single pulses with fluences in the range of 0.8 – 3.0 J/cm², same spot size) produced no observable changes. Therefore, limiting the dissipation of heat from the laser-heated spot to predominantly lateral (2D) transfer within the Si film is a critical condition and requires irradiated/melted spot size that is comparable to or in the order of the heat diffusion length (about 1.5µm) [11]. Another important factor is that Si has higher density (ρ = 2.52g/cm³) in its liquid state than in its solid state (ρ = 2.32g/cm³ for crystalline Si and ρ = 2.2 g/cm³ for amorphous Si [13]). The dynamics and the geometry of this solidification process, is responsible, at least as a first approximation, for the formation of the tips. Due to the lateral heat dissipation, the periphery of the spot is more rapidly cooled and have lower temperature than the spot’s central region. Thus the freezing front moves from the edges to the center and pushes the remaining liquid silicon toward the center. This process of fast displacement of liquid silicon toward the center is strongly enhanced by the fact that the solidified material occupies larger volume. It results in the formation of a jet, or a nano-jet, of liquid that erupts and, upon complete solidification, forms these remarkable, sharp conical tips.

The above-described mechanism can be expected to work in an irradiated area geometry in which only one size is comparable to the heat diffusion length. A mechanism for formation of sharp ridges associated with movement of liquid caused by the moving solidification front has been suggested in [14] to explain periodical surface structures on laser-annealed germanium. The predicted profile is remarkably similar to what we observe in our experiments (Fig. 4a). We tested this case by using slit projection masks with width that were comparable to the diameters of the pinhole masks used earlier. Fig. 4 shows AFM images of structures that were obtained upon using slits with 3 different widths on a 200nm Si-film SOI sample. It can be seen that in the case of slit widths of 25 and 50µm (producing laser lines with widths 2.8 and 5.6 respectively) ridge structure forms. These ridges have apical radii of curvature in the range 50-100nm, i.e. they are nano-ridges. The slit with width 100µm (Fig.4c) did not produce a ridge structure, but rather an ablated line with slightly raised edges. Two other observations need to be mentioned: the threshold for surface changes when using a slit with width 50µm is 0.7 J/cm², i.e. slightly lower than that for a circular spot with the same diameter; the fluence range within which nano-ridges form is very narrow – just 0.1- 0.2Jcm² above the threshold and at higher fluences, the ridges break into ridge-valley-ridge structure (not shown), which would be the analog to the crater.

![AFM images of structures fabricated with single pulses and slit masks: (a) illuminated line width 2.8µm and fluence 1.13 J/cm²; (b) illuminated line width 5.6 and fluence 0.93 J/cm²; (c) illuminated line width 11.2 µm and fluence 0.87 J/cm².](image-url)
formation in the circular geometry case. The importance of the 2D heat transfer to the formation of these nano-structures is indirectly demonstrated by these two observations. First, the lower threshold for line geometry compared to that for circular spot geometry is due to the fact that ratio of the heat-conducting surface (defined by the film thickness) to the volume of the melted material is smaller for the line geometry than for the circular spot geometry and heat dissipation is less effective in the former case. Second, the narrower fluence range of nano-ridge formation compared to the range for nano-tip formation also has to do with the effectiveness of heat dissipation: in the former case, only a small additional laser energy is enough for the system to reach conditions for liquid ejection from the center region, whereas it takes much more for this to happen in the latter case due to a more effective heat loss mechanism.

CONCLUSIONS

We have found conditions for the formation of nano-tips and nano-ridges on single-crystal Si films with thicknesses from 0.2 to 1.1 µm on silica or oxidized silicon substrates by single-pulse irradiation with KrF excimer laser radiation. The estimated threshold values and the formation dependence on film thickness and irradiation spot/line sizes can be explained in the frame of a simple, qualitative model for the mechanism of formation that is dominated by 2D heat transfer and solidification-front-driven movement of melted material.

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REFERENCES