Fabrication of Dot-like Nano-protrusions on Silicon Surfaces Using Nanosecond Pulse Nd: YAG Laser Irradiation

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Abstract

An array of Nano-protrusions (NPs) was fabricated on silicon surfaces in air and a low pressure environment using pulsed laser irradiation. The uniformly sized NPs were linearly aligned at a low laser energy density, which is typically a few kilojoules per square meter. The linear array of NPs appeared perpendicular to the laser polarization vector \(\mathbf{E}\), and the interval of the NPs lines was almost equal to the wavelength of the incident laser. The primary NPs grew epitaxially and were covered with an oxide film layer, which was determined by means of a structural and elemental analysis using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS). We propose a nano-patterning fabrication method using the laser-induced NPs alignment based on a microscopic structural analysis.

Keywords: Laser-induced Periodic Surface Structure (LIPSS), Silicon Protrusion, Conical Structure, Self-organization, Nano-patterning

1. Introduction

Laser-induced nano structures on material surfaces have long been studied for various materials (metals, semiconductors, ceramics, and polymers) [1–6] because of their expected applicability to opto-electronic devices such as solar cells and phototransistors due to their characteristic luminescence.[7–9] In particular, laser-induced micro-protrusions, such as columns and cones, have been widely studied.[4–6]

On the other hand, beam irradiation often induces the self-organization of ordered structures on given surfaces.[10–14] For example, an explanation that has recently been proposed for sub-wavelength LIPSS bifurcations is the self-organization of the surface instabilities arising from competition between the two processes of surface roughening due to explosions and surface smoothing due to self-diffusion.[11] In this paper, we report that dot-like nano-protrusions (NPs) are self-organized in a linear array after pulsed laser irradiation. The present surface NPs are considered those of the micro-protrusion at nano sizes.

Most of the previous experiments on laser-induced surface protrusions were conducted in a vacuum or inactive gas environment.[1, 2, 12–14] We compared the differences in laser irradiation between air and a low-pressure environment for NP-array fabrication, because pulsed-laser irradiation in air is expected to be a fast and easy method without the need for pressure control. In this study, we report on the linearized NPs fabricated on Si (100) at a low laser energy density, typically less than 5 kJ/m², in air and in a low-pressure environment. After irradiation, we carried out a microscopic investigation of the laser-induced surface structures, and report that the smaller NPs (hereafter, denoted as primary NPs) grew epitaxially and were covered with oxide film layer.

2. Experimental Methods

Our specimen was an n-type Si (100) substrate (KN Platz Co., Ltd.) with a resistivity of 22–45 \(\Omega\)-cm. Laser irradiation was carried out at room temperature in a low pressure (1.33 Pa) environment inside a vacuum chamber, and in air using a Nd: YAG pulsed laser (Inlite II Continuum co., Ltd.) at a 532-nm wavelength, a pulse width of 5–7 ns,
and a repetition rate of 2 Hz. The laser incident condition was determined by arranging the polarizer and half-wavelength plate between the laser source and the specimen (Figure 1). In this study, the laser incident beam (beam diameter of 6 mm) was adjusted for an average power of 1.24 kJ/m² at the surface. After irradiation, the surface morphology of the specimens was observed using high-resolution scanning electron microscopy (SEM: JEOL-JSM6500), and the internal structure was observed using transmission electron microscopy (TEM: JEOL 2010F). The thin foil specimens for TEM observation were prepared using ion milling and a focused ion beam (FIB) process.

3. Results and Discussion

Figure 2 shows SEM images of the NP arrays evolved on the Si surface after laser irradiation at a 1.24 kJ/m² average power in a low pressure (1.33 Pa) environment: (a) 1000 pulses; (b) 3000 pulses; (c) 6000 pulses; and (d) 9000 pulses. In Figure 2(a), after 1000 pulses, the dot-like protrusions, viz. primary NPs, were produced on the Si surface. In Figures 2(b) and 2(c), from 1000 to 6000 pulses, the primary NPs were linearly aligned and had grown into larger NPs. The size of the NPs was 20–80 nm in Figure 2(b). In Figure 2(c), some of the NPs that were close to each other begin to combine to form larger bodies and this tendency continues, as shown in Figure 2(d), depending on the number of laser pulses. We summarize, in Figure 3, the diameter distributions of the NPs measured from the SEM photos in Figure 2. It can be seen that the larger NPs have a hemispheroidal shape (hereafter, denoted as hemispheroidal NPs). The growth of the NPs depended on the number of laser pulses. It is suggested that the primary NPs can grow into hemispheroidal NPs when a large number of laser irradiations are used. If one continues the irradiation, the NPs might develop into even larger micrometer-sized bodies, such as micro-columns and micro-cones.[4–6]

The linearized NPs array was perpendicular to the laser light polarization, and the ripple period, Λ, was close to the central laser wavelength of 532 nm, according to the equation given in [2]

\[ \Lambda = \frac{\lambda}{1 \pm \sin \theta}. \]  (1)

where \( \lambda \) is the incident laser wavelength and \( \theta \) is the angle of incidence of the laser beam. In this study, the incident wavelength was 532 nm, so \( \theta = 0 \) and \( \Lambda = \lambda \). In Fig. 2, the intervals of the ripple lines at 500 nm were smaller than the incident laser wavelength because the specimens were slightly tilted (± 5°). The present study suggests that the
patterning of uniformly aligned NPs that depend on the laser wavelength is possible by means of controlling the laser irradiations, which may include changing of the incident laser angle.

The high-resolution TEM image in Figure 4(a) is a cross-section of a primary NP grown on the Si (100) surface after irradiation of 9000 pulses in low pressure, and shows that the primary NPs have a conical shape and a size of about 20 nm. The crystallinity of primary NPs corresponded to those of the bulk silicon. The inset in Figure 4(b), which is the diffraction pattern taken from bulk Si that includes the primary NP, indicates that the NP has the same crystalline orientation as the substrate, viz. its epitaxial growth. The EDS point analysis in Figure 4(c) [taken from point (c) in Figure 4(a)] shows that the primary NP is mainly composed of silicon. The excess growth of the silicon oxide layer was not recognized on the surface of the primary NP. Note that the carbon peak in Figure 4(c) originates from the protection layer of the ion milling process.

Figure 5(a) shows a cross-section of a hemispheroidal NP, which was induced by 9000 laser irradiations in a low-pressure environment. The diffraction pattern in Figure 5(b), which was taken from the hemispheroidal NP (including Si bulk), shows that it was not grown epitaxially, and it was made of microcrystals of silicon. Figure 5(c) shows an EDS point analysis of the hemispheroidal NP [taken from point (c) in Figure 5(a)]. The total size of the hemispheroidal NP was approximately 200 nm. No excess growth of the silicon oxide layer was recognized on the surface and inside of the hemispheroidal NP.

The array of primary NPs can be fabricated using laser irradiation in air. Figure 6 shows a SEM image of a well-

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**Fig. 4** TEM observation and EDS analysis of 9000 pulses at low pressure: (a) The high resolution TEM image of primary Nano-protrusions (NPs); (b) Diffraction pattern taken including NP; (c) EDS point analysis (indicated by arrows in Figure 4(a)).

**Fig. 5** TEM observation of 9000 pulses at low pressure: (a) Cross section of hemispheroidal Nano-protrusions (NPs); (b) Diffraction pattern taken of hemispheroidal NP; (c) EDS point analysis of hemispheroidal NP, which is indicated by arrows in Figure 5(a).

**Fig. 6** SEM image of NP array laser irradiated to 1500 pulses in air.
aligned NP array fabricated in air on a Si surface using laser irradiation. It turned out that under the same laser conditions carried out in a low pressure environment, we needed only 1500 laser pulse irradiations. This is because there was a difference in the growth rate between that in a low-pressure atmosphere and that in air. The aligned NPs, as shown in Figure 6, were formed in air as well as in the low-pressure environment and the linearized NP arrays are perpendicular to the laser light polarization.

Figure 7(a) shows a high-resolution TEM image of a NP observed on a Si (100) surface after irradiation in air with 1500 pulses at 1.24 kJ/m². The crystallinity of primary NP in air also corresponded to that of the bulk silicon. The inset in Figure 7(b), which is the diffraction pattern taken from bulk Si including the NP, indicates that the NP has the same crystalline orientation to the substrate viz. its epitaxial growth. Figure 7(c) shows an EDS point analysis of the bulk portion underneath the NP [taken from point (c) in Figure 7(a)], which is mainly composed of silicon, while Figure 7(d) displays the EDS analysis of point (d) in Figure 7(a). The surface just above the NP shows that the sample part is composed of silicon and oxygen. Note that the carbon and copper peak originates from the carbon deposited protection layer for the FIB process and the copper microgrid for the TEM observation.

The size of the primary NPs was about 15–20 nm and they were grown epitaxially in a low-pressure environment and in air (in Figures 4 and 6). It can be concluded that the fabricated NPs were covered with a thin silicon oxide (probably SiO₂) layer of a few nanometers, because the oxygen peak increased at the surface in Figures 7(c) and (d). However, the excess growth of the silicon oxide layer was not found on the surface of the NPs produced in air. This implies that NP production in air is possible without needing a reduced-pressure environment.

4. Conclusion
A linear array of 15–20 nm primary NPs was fabricated on Si (100) substrates in air as well as in a low-pressure using a single-laser irradiation method. The epitaxially grown primary NP can grow to become hemispheroidal NPs that are approximately 200 nm or more by using a large number of laser irradiation repetitions. This suggests that the nanosecond pulsed laser irradiation method can be used for nano-patterning fabrication on a laser-wavelength scale via the laser-induced alignment of the NPs, which may include a changing of the incident laser angle. We expect that opto-electronic devices with patterned NPs can be developed using the present laser-irradiation technique.

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