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Nanosecond pulsed laser induced

self-organized nano-dots patterns on GaSb surface

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Abstract

We report a technique for formation of two-dimensional (2D) nanodot (ND) patterns on gaillium antimoide (GaSb) using a nanosecond pulsed laser irradiation with 532 nm wavelength. The patterns have formed because of the interference and the self-organization under energy deposition of the laser irradiation, which induced the growth of NDs on the local area. The NDs are grown and shrunken in the pattern by energy depositions. In the laser irradiation with average laser energy density of 35 mJ cm^{-2}, large and small NDs are formed on GaSb surface. The large NDs have grown average diameter from 160 to 200 nm with increase of laser pulses, and the small NDs have shrunken average diameter from 75 to 30 nm. The critical dot size is required about 107 nm for growth of the NDs in the patterns. Nanosecond pulsed laser irradiation can control the self-organized ND size on GaSb in air as a function of the laser pulses.

Keywords: Nanosecond pulsed laser irradiation, Self-organization, Nanodots patterns, Gallium antimonide,

1. Introduction

Nanostructure such as nano-dots (NDs) has been attracted interest due to the enhancement in functional properties and their potential applications. The nanostructures using some beam processes such as electron [1, 2], ion [3, 4], molecular [5–9] and laser [10–18] was reported by their experimental observations. In particularly, a pulsed laser irradiation has been also achieved surface damage pattern at nanoscale on material surface with a wavelength-dependent periodicity by the interference of laser lights [19–26]. In addition, the experimental observations have revealed that nanosecond pulsed laser irradiation induced a self-organization due to the thermal effect [14–16]. In an iron-aluminum alloy surface, it was clear that the periodic pattern ordered along a particular in plane direction on crystal surface with increase of laser pulses [16].

Recently, we demonstrated that periodic NDs were formed with the interference of laser lights and the self-organization under the nanosecond pulsed laser irradiation. Although it has been well discussed the self-organization on/in a crystalline by some processes [3, 4, 6–8], it is unclear the dimension and the size of the NDs on/in a crystal surface under an energy deposition of nanosecond pulsed laser irradiation. In this study, we focus on the self-organization of the NDs on the local area of GaSb surface under the thermal effect of pulsed laser irradiation, because it has been well known that self-organization is occurred in

GaSb by a thermal effect. The structural and chemical analysis is investigated using a scanning electron microscopy (SEM), a transmission electron microscopy (TEM) and a scanning transmission electron microscopy (STEM). We have demonstrated the use of a laser beam technique enables the control of the dimension and the NDs size on GaSb (100) substrate.

2. Experiment

The sample used in this study is a commercially available surface-polished GaSb(100) wafers. The samples were irradiated at room temperature in air environment using a Nd: YAG pulsed laser (Continuum Co., Ltd. Inlite II) with a wavelength of 532 nm, a pulse width of 5–7 ns, and a repetition rate of 2 Hz. The laser beam diameter was 6 mm [14–17]. The formation of the NDs patterns were performed by the laser irradiation with average laser energy density of 35 or 124 mJ cm^{-2}.

After laser irradiation, we performed SEM for the size distributions using a JEOL JSM-7001FA at acceleration voltage of 15 kV. Fast Fourier transform (FFT) was employed to convert SEM images to the 2D autocorrelation function (ACF) images. For the ACF images extracted from the SEM images, the contrast and brightness were adjusted in order to emphasize the positive parts of the large NDs. Back-scattered electron image for composition (COMPO) and energy dispersive X-ray (EDX) mapping images were measured at acceleration voltage of 5kV using SEM equipment. Then, TEM observations and STEM-EDX analysis for internal structure were performed using JEOL JEM-2010F and Hitachi HD-2000 with EDX system at an acceleration voltage of 200 kV. The irradiated surface protected by thicker carbon and thin heavy atom (for example, Pt and W) layers deposition before TEM specimen preparation. The thin foil specimen for the cross sectional analysis was prepared using a focused ion beam (FIB: Hitachi FB-2100).

3. Results and discussions

Figure 1 shows SEM images of a formed NDs patterns on the GaSb surface after pulsed laser irradiation of 10–100 pulses at an average energy density of 35 mJ cm^{-2}. The NDs patterns were observed on the local area, where is more than 100 μm^2, as shown in Fig. 1(a)–(d). As shown in Fig. 1(a), the NDs pattern on the surface consists of small and large NDs that formed randomly at 10 pulses. Subsequently, the interval between NDs is decreased at 25 pulses, as shown in Fig. 1(b). In Figs. 1(c) and (d), the aligned NDs patterns are formed at periodic intervals. Although the aligned NDs are not straight line, the directions are found along 〈011〉 direction, which were almost equal perpendicular or parallel to the polarization of irradiated laser lights [17]. To evaluate the periodicity of the large NDs pattern, the average interval between NDs was analyzed with 2D-ACF images as shown in Fig. 1(e)–(h). The bright spots indicate the average ND positions. As shown in Fig. 1(e), the intervals between NDs were broad and random after 10 pulses, but subsequently became narrower as the interval decreased with 25 pulses in Fig. 1(f). The NDs had a subwavelength separation of approximately 265 nm. As shown in Fig. 1(g), the periodic interval appeared with approximately 530 nm of the x direction after 50 pulses. After 100 pulses, the large NDs interval along the y direction became approximately 530 nm, as shown in Fig. 1(h). It is supposed that the light is scattered by a ND under nanosecond pulsed laser irradiation, and the interference of scattered lights attributed to the formation of the NDs patterns because the ND patterns were exhibited from a half-wavelength to wavelength of irradiated laser beam.

We carried out SEM-COMPO and SEM-EDX analyses of irradiated sample after 100 pulses in air to investigate the concentration maps of gallium (Ga), oxygen (O), and antimony (Sb) in Figs. 2(a)–(d). The phase decomposition involving patterned nanostructure thought Ga oxidation and Sb releasing because the concentration of Ga and O are high at the ND region. It is suggested that the liquid Ga diffuses into surface damages during the laser irradiation.

Moreover, we carried out a TEM observation and STEM-EDX analysis to investigate the internal structure of aligned NDs. The aligned NDs pattern has formed in air at 124 mJ cm^{-2} after 50 pulses as well as 35 mJ cm^{-2} after 100 pulses. Figure 3(a) shows the cross sectional TEM image of the large NDs along the x direction. The large ND was about 20 nm in height from the surface, and the pit was 65 nm in depth. From the shape of the nano-dot/pit, it is reasoned that the liquid phase minimize the surface energy, when heated by nanosecond pulsed laser irradiation. Figures 3(b)–(e) show EDX mapping images of carbon (C), Ga, O, and Sb. The upper layer on the nano-dot/pit surface has high C distribution because of C deposition after the laser irradiation. There is no Ga distribution in the upper layer as shown in Fig. 3(c). The implantation of Ga atoms during FIB process is not occurred, because the ND protected by deposition of thicker C and thin Pt layers before TEM sample preparation. According to SEM-EDX mappings, the distribution of O atoms is greater at the ND region than that at the GaSb surface region. From these results of chemical analysis, revealing the shape and elemental concentrations. The shape of nano-pit suggests self-assembly of damages pattern under the laser irradiation [18], and the concentrations of Ga and O supposed due to oxidation during laser heating and cooling. The result that is supported by SEM-EDX and STEM-EDX data showing no Sb in the ND, the loss of Sb would result in Ga NDs formation because Ga diffuses faster than Sb in

GaSb [27], and Sb atoms on the surface would be evaporated in air by heating during laser irradiation, then leaving Ga atoms segregate and oxidize in air. Thus, it may be that the pits are result of assembling of surface defects. Then, the laser irradiation induced the pits pattern, where are grown ND due to stable position.

Figure 4 shows a histogram of the dot diameter size distribution at different irradiation times of 10 pulses, 25 pulses, 50 pulses, and 100 pulses, respectively. The size distribution of the NDs was measured to determine the dot size. Case of an ellipse, after addition the minor axis and major axis values of ND and then divided by 2. In Fig. 4(a), the NDs diameter ranges from 20 to 240 nm, and the peak is at approximately 100 nm. The boundary of small/large NDs is determined to 140 nm by the redaction frequency in the distribution. After 25 pulses, it becomes narrow and the peak shifts to smaller values, as shown in Fig. 4(b). As shown in Figs. 4(c) and (d), two peaks are present in the histograms after 50 and 100 pulses. The distributions of 0–140 (small) and 140–290 (large) nm were observed. The enlarged frequency data of larger NDs is shown as an inset in the region of 130–290 nm. The left peak is decreased to 40 nm, and the right peak is increased to 200 nm by the laser irradiation in Figs. 4(b)–(d). From the distributions, the decrease and increase of the diameter in size are manifested. Figure 5 shows the relationship between the average diameter of small and large NDs and number of laser pulses. The averages of both the smaller and larger NDs from two distributions was plotted (error bars represent the standard deviation), and the average diameter of the small NDs decreased from about 75 to 30 nm with increased laser pulses, and the large NDs increased from about 160 to 200 nm. This indicates that the small NDs shrank while the large ones grew further, yielding a bimodal dot size distribution. Therefore, the critical dot size in the nanostructured microstructure can be classified as the intersection of the two lines (yellow and gray dashed lines; $D_{large} = 0.505 \cdot n + 152.55$ and $D_{small} = -0.428 \cdot n + 67.83$) of 106.7 nm from the equation, the lines of equation were calculated from plots of D by least-squares, where D is average of NDs, n is number of laser pulses. It is determined that the critical dot size become about 107 nm from the intersection of the lines under nanosecond laser irradiation at 532 nm. The small NDs is first produced locally by ablation and/or melting by the laser heating. The NDs are smaller than the critical dot/pit size shrink or/and disappear due to energy deposition of the pulsed laser irradiation. The process is similar to Ostwald ripening where the small NDs are merged with the large ones [28]. Thus, it is expected that nanosecond pulsed laser induced self-organized NDs in the pattern can also control the size as a function of the number of laser pulses.

4. Conclusions

The nanopatterns of self-organized dots/pits have formed after nanosecond pulsed laser irradiation up to 100 pulses of 35mJ cm^{-2} and 50 pulses of 124 mJ cm^{-2}; these nano-dots/pits on the GaSb surface have periodicity at a certain direction.

The intervals of nano-dots/pits have changed to nearly 530 nm with increase of laser pulses. Furthermore, the change has occurred through the growth and shrinkage of NDs. The large NDs have grown average diameter from 160 to 200 nm and the small NDs have shrunken average diameter from 75 to 30 nm. The critical dot diameter required for the growth of ND has estimated to be about 107 nm under nanosecond pulsed laser irradiation. Thus, nanosecond pulsed laser irradiation can control the NDs size as a function of the number of laser pulses. The simple technique of NDs patterns could be useful for fabrication of nano- and micro-materials.

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Figure captions

Fig. 1. SEM images of the local surface areas after laser irradiation with average energy density of 35 mJ cm^{-2}; (a) 10, (b) 25, (c) 50, and (d) 100 pulses, respectively. (e)–(h) the 2 D - ACF images obtained from SEM images in (a)–(d).

Fig. 2. SEM-COMPO and SEM-EDX mapping images of (b) gallium, (c) oxygen and (d) antimony after laser irradiation for 100 pulses at 2 Hz in air, and at an energy density of 35 mJ cm^{-2}.

Fig. 3. TEM image and STEM-EDX analysis of NDs on a GaSb surface after laser irradiation for 50 pulses at 2 Hz in air, and at an energy density of 124 mJ cm^{-2}. (a) Cross-sectional TEM image of the x direction. (b)–(e) STEM-EDX mapping images of (b) carbon, (c) gallium, (d) oxygen and (e) antimony. The upper layer of nanodot surface has high carbon concentration, as shown in Fig. 3(b), because of the carbon deposition for damage protection from gallium ion beam.

Fig. 4. Histograms of ND diameters from the SEM images shown in Figs. 4 (a)–(d); M and σ^2 are the average and standard deviation, respectively. The ND diameter ranged from 20 to 240 nm. The enlarged frequency data from 140 to 290 nm are shown in (b) to (d).

Fig. 5. The relationship between the average ND diameters (error bars represent the standard deviation) and number of laser pulses.

Figure

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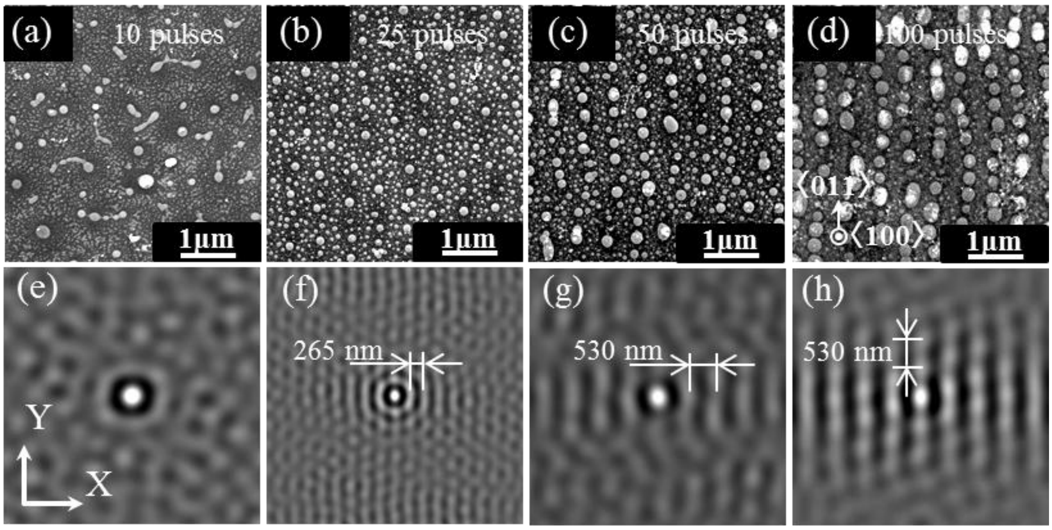

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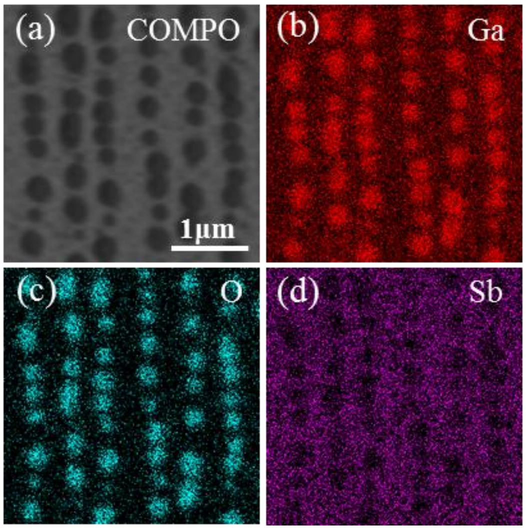

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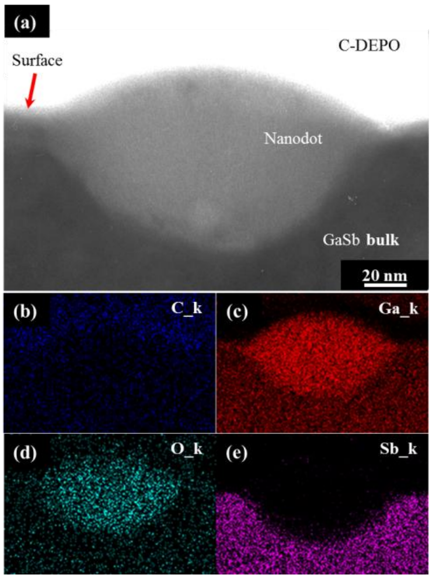

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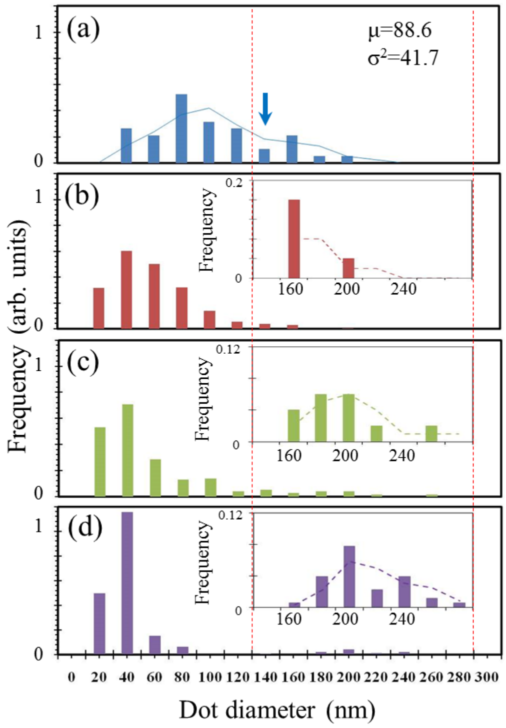

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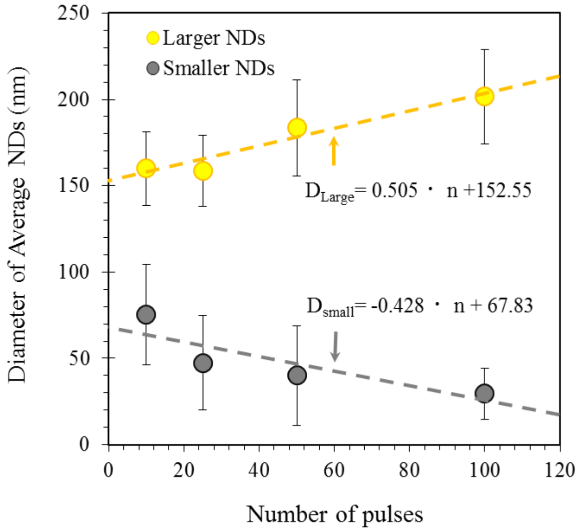

Fig. 5. Yoshida