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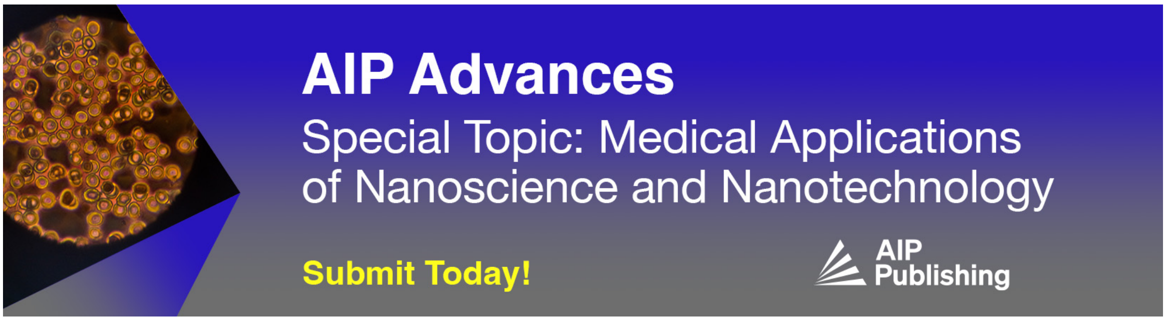

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ABSTRACT

Although deforming a silicon single crystal at a temperature of about 600 °C lower than its melting point (1414 °C) by direct electrical heating was successfully demonstrated, the mechanism has still not been fully clarified. In this paper, we propose a model for the low temperature deformation of a semiconductor single crystal by direct electrical heating. The thermographic observation during direct electrical heating reveals that the local temperature is higher at the region where dense dislocation occurred in the semiconductor single crystal by uniaxial pressing. This is interpreted in terms of the scattering of an electron by the dislocation leading to an increase in the electrical resistivity. Finally, the deformation temperature of the semiconductor single crystal apparently becomes low due to the occurrence of such hot spots. We have also demonstrated an application to mold a microlens array composed of a germanium single crystal with a focal length of 25 μm.

INTRODUCTION

It is well known that semiconductors such as silicon (Si) and germanium (Ge) are brittle materials because they have strong chemical bond anisotropy. However, it was reported that a Si single crystal can be plastically deformed by raising its temperature to around its melting point (1200–1405 °C).[1,2] Recently, plastic deformation of ZnS single crystals in darkness at room temperature has also been reported.[3] We have also demonstrated the deformation of the Si single crystal at a temperature of about 600 °C lower than its melting point (1414 °C) by direct electrical heating with a pulsed current.[4] Until now, however, the mechanism of the deformation of the Si single crystal at a temperature hundreds of degrees below its melting point by direct electrical heating has not been fully understood. The phenomenon in which the plastic deformation or dislocation movement is promoted by the electric current has been reported for alloys and phase change materials and is called the electroplastic effect.[5–7] Such an electroplastic effect is mainly explained by the following two models. The first model is that the electrons are scattered by dislocations and the dislocations become locally hot.[6] The second is that the electrons collide with dislocations and give the dislocations momentum, which is called the electrical wind force.[7]

Meanwhile, since mid-infrared to far-infrared light is widely used for not only identifying chemical substances but also measuring the temperature of an object, research regarding light sources and detectors has been actively progressed.[8–10] For the lens of the infrared light detector, an infrared transmitting material, such as silicon, germanium, or chalcogenide glasses, is used. Although the chalcogenide glass has the advantage of easy processing,[11–13] it is known that it has a smaller refractive index compared to those of Si and Ge crystals.[14] Furthermore, the chalcogenide glass often contains toxic As and Se, and the glass transition temperature is as low as 200–400 °C. On the other hand, Si and Ge single crystals exhibit excellent optical properties in the infrared wavelength region. However, as described above, since they are brittle materials, their lenses are conventionally fabricated by cutting and polishing rather than press molding. Therefore, it is difficult to process them into a complex shape, such as a microlens array. From an industrial standpoint, it is important to provide a manufacturing method for molding the Si or Ge single crystal into a complex shape. In particular, a microlens array is considered to be very useful because decrease in the quantity of light according to the downsizing of a photodetector can be overcome. Previously, we have demonstrated the fabrication of a single lens composed of Si by press molding with direct electrical heating, but have not yet fabricated a microlens array.[4] Furthermore, although a Si microlens can be fabricated by photolithography using a grayscale mask and dry etching, it is difficult to form a spherical shape.[15]

In this paper, we propose a model for the low temperature deformation mechanism of the Si single crystal by direct electrical heating. In addition, we demonstrate a possible application of the fabrication method of a microlens array composed of a Ge single crystal by uniaxial pressing with direct electrical heating.

EXPERIMENTS

Commercially available CZ-Si (6 × 6 × 6 mm^3) and CZ-Ge (6.0Φ × 4.0 mm^2) single crystals were used in the experiments. The dopant for CZ-Si is phosphorus, and its resistivity is 4.29 Ω cm at room temperature. The dopant for CZ-Ge is antimony, and its resistivity is 20.5 Ω cm at room temperature. Spark plasma sintering (Sinter Land; LABOX-125, SPS) equipped with a uniaxial pressurizer, electrodes, a vacuum chamber, a pulsed DC generator, a displacement measuring device, a temperature measuring device, a preheating unit, and a pressure measuring device was used. A schematic view of the SPS system is shown in Fig. 1. The pressing direction was set to be <110> for Si and <100> for Ge. We determined the crystal orientation based on the flat orientation of an ingot and cut the samples from the ingot. Previously, we have confirmed that the shape and deformation amount depended on the crystal plane to be pressed.[4] Although the pressing condition is the same for every experiment, differences in the shape and deformation amount were observed for the deformed Si single crystal after pressing along [100], [110], and [111] axes. Details have been reported in Ref. 4. On the side surface of the (110) sample, a region with many slip lines and a region with few slip lines were observed. To observe local heating around dislocations originated from the formation of slip lines, we have selected the (110) plane as the pressed plane for the Si single crystal. In addition, since Si and Ge have the same slip plane, they are considered to exhibit a similar deformation behavior. In the Ge microlens array fabrication experiments, since the pattern on the Si mold is a cylinder, it is preferable that Ge is deformed into a circular shape. Furthermore, it is preferable that the deformation amount of Ge is large. From the above, it is considered that the (100) plane is suitable for fabricating the Ge microlens array due to the isotropic and large deformation.

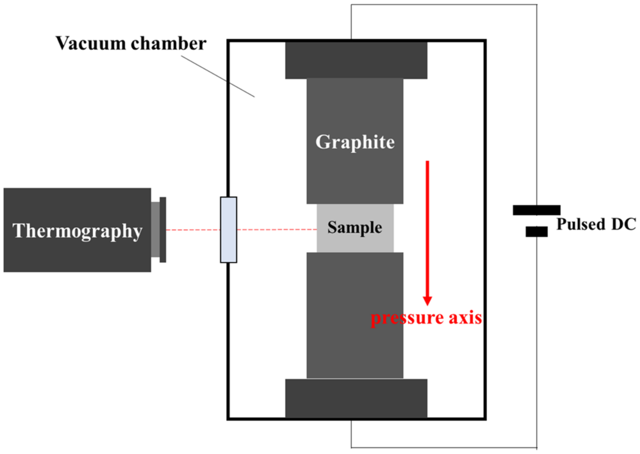

FIG. 1. Schematic view of the SPS system.

To measure the temperature distribution of the Si single crystal during direct electrical heating, a cubic sample was used and observed from the $(1\bar{1}0)$ plane by thermography (CHINO; FLIR A310). The sample was sandwiched by graphite electrodes (15Φ × 25 mm^2) and set in a chamber of SPS. After the inside of the chamber was exhausted to 20 Pa, the sample was heated to 340 °C by a pre-heating unit. The window material is BaF$_2$. Thereafter, the temperature of the sample was increased up to the prescribed target temperature by applying a pulsed DC current. To increase the contact area between the sample and the graphite electrodes, a uniaxial pressure of 14.1 MPa was initially applied. The temperature of the sample was measured by thermography and was controlled by adjusting the current and the voltage. After the temperature of the sample reached the target temperature, the uniaxial pressure was applied while maintaining the temperature. Then, the temperature and the uniaxial pressure were maintained for 10 min after reaching the target uniaxial pressure. Finally, the uniaxial pressure was released, and the sample was cooled down to room temperature by stopping the pulsed DC current. Table I summarizes the experimental conditions.

After the plastic deformation of the Si single crystal sample, the slip lines of the $(1\bar{1}0)$ plane were observed with an optical microscope. To reveal the detailed structural change, bright field TEM observation was performed after milling the sample from the $(1\bar{1}0)$ plane. To reveal the variations of the electrical resistivity and temperature distribution after plastic deformation, the deformed Si sample was heated again to 1000 °C by direct electrical heating.

To evaluate the infrared transmittance of the plastically deformed Ge sample, the plane perpendicular to the pressing axis was mirror-polished to the thickness of 2 mm, and then the infrared spectrum of the sample was measured by FT-IR (PerkinElmer; Spectrum Two) at room temperature. In addition, to observe the detailed structural change in the plane parallel to the pressing axis by FE-SEM (JEOL; JIB-4600F), a part of the Ge sample was cut and polished along the pressing axis to a tabular piece.

In the microlens array fabrication experiments, the Ge single crystal (6.0Φ × 1.5 mm^2), in which the (100) plane was mirror-polished, was used as a sample. The mold for the microlens array was prepared by the Si single crystal (6.0Φ × 4.0 mm^2). The pattern of nine cylinders with a diameter of 20.0 μm and a depth of 5.14 μm was fabricated on the mold of the Si single crystal by FIB milling (JEOL; JIB-4600F). A stack of the Ge sample and the Si mold was

TABLE I. Experimental conditions.

Sample	Preheating temperature by heater (°C)	Target temperature (°C)	Heating rate (°C/min)	Uniaxial pressure (MPa)	Uniaxial pressure rising rate (MPa/min)	Retention time (min)
Si	340	1000	48	111	35.4	10
Ge	340	500–700	48	70.7	35.4	10

sandwiched by graphite electrodes and treated by direct electrical heating. The experimental conditions were as follows: temperature of the Ge sample: 650 °C, applying uniaxial pressure: 70.7 MPa, and holding time: 10 min. After the uniaxial pressing with direct electrical heating, the shape of the plastically deformed Ge sample surface was evaluated with an AFM (Bruker; Multimode8). The function of the microlens array was also confirmed by using a homemade infrared wavelength transmission microscope equipped with an infrared lamp (BHK; 72-010008) and an InGaAs CCD camera (Hamamatsu; C10633).

RESULTS AND DISCUSSION

Figure 2(a) shows an optical microscope image of the cross-sectional plane of $(1\bar{1}0)$ parallel to the pressing axis in the plastically deformed Si single crystal sample. Many slip lines were observed at the four edges (region B) compared to the middle part (region A) in the $(1\bar{1}0)$ plane. To reveal the dislocation density in each region, bright field TEM observation from the <001> direction was performed [Figs. 2(b) and 2(c)]. From the EELS measurements, we confirmed that the thicknesses of the regions A and B in samples were 312 nm and 340 nm, respectively. Although there is a slight difference in the sample thicknesses, it is clear that the dislocation density for region B is much higher than that for region A, namely, region B with many slip lines includes a large amount of dislocations.

The temperature distribution of the Si single crystal sample before and after deformation during direct electrical heating was observed by thermography [Figs. 2(d) and 2(e)]. Due to the heat transfer from the sample to the graphite electrode, a temperature gradient was created from the center to up and down in the sample. Interestingly, the temperature of region B containing many dislocations was locally hot and higher than that of region A by approximately 25 °C. We have also confirmed the electrical resistivity of the Si sample before and after deformation under various temperatures [Fig. 2(f)]. The electrical resistivity of the deformed Si sample was clearly increased and became more than that of the pristine Si single crystal. A possible reason for the increase in the electrical resistivity caused by the creation of a dislocation in the crystal structure could be interpreted in terms of the electron scattering. It is known that the electrons can be scattered by the charged dislocation.[16–18] The dislocations in a semiconductor crystal can form

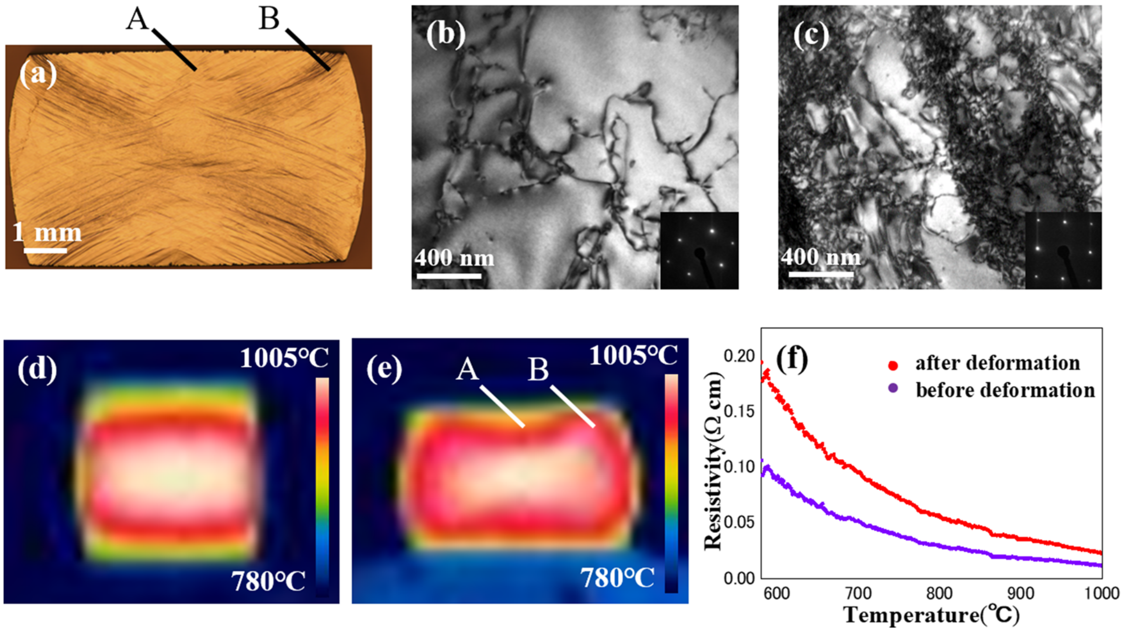

FIG. 2. (a) Optical microscope image of the $(1\bar{1}0)$ plane of deformed Si, bright field TEM image of (b) region A and (c) region B, (d) temperature distribution of Si before deformation observed by thermography, (e) after deformation, (f) electric resistivity of Si before and after deformation.

an energy level in the bandgap and be charged by trapping carriers, leading to the increase in electrical resistivity at room temperature. However, at high temperatures, the dislocations are generally not charged, and finally the electron scattering by the charged dislocations is not dominant. In our experiments, we considered that the electron could be scattered by the strain field generated around the dislocation.[19,20]

Let us consider the model for the low temperature deformation of the semiconductor single crystal under uniaxial pressing with direct electrical heating. In the initial stage before applying uniaxial pressure, the sample temperature was kept at 1000 °C by the Joule heating of the sample itself induced by a pulsed DC current. In the next stage after applying the uniaxial pressure, a large amount of dislocations was created, and then the temperature of such a region in the crystal was increased locally due to the higher electrical resistivity. Salandro *et al.* proposed a model in which the drift electrons were scattered by dislocations and the dislocations were locally hot.[6] Furthermore, it is known that the dislocation velocity increases with an increase in the temperature.[21] In the case of the semiconductor crystals such as Si and Ge, the brittle–ductile transition is also governed by the dislocation velocity, that is, the temperature.[22,23] Therefore, even if the sample center temperature is low, the semiconductor is plastically deformed if the dislocation temperature is high. The temperature, we measured by thermography is the sample center temperature. Without the pulsed current, no hot spots would appear. With the pulsed current, the dislocations scatter electrons and become locally hot. From the above, it is considered that even when the sample center temperature is the same, the dislocation temperature is higher with the pulsed current than that without the pulsed current. We think that this allows for low temperature deformation of the semiconductor single crystal.

We think that the proposed low temperature deformation mechanism could be applied to both single crystals of Si and Ge. The phenomenon that dislocations scatter electrons and become locally hot can occur in both Si and Ge. Although Si and Ge have different lattice constants, melting points, and bandgaps, these differences are unlikely to affect the low temperature deformation mechanism. We selected the Ge crystal as a starting material of the microlens array due to ease of deformation compared to the Si crystal.

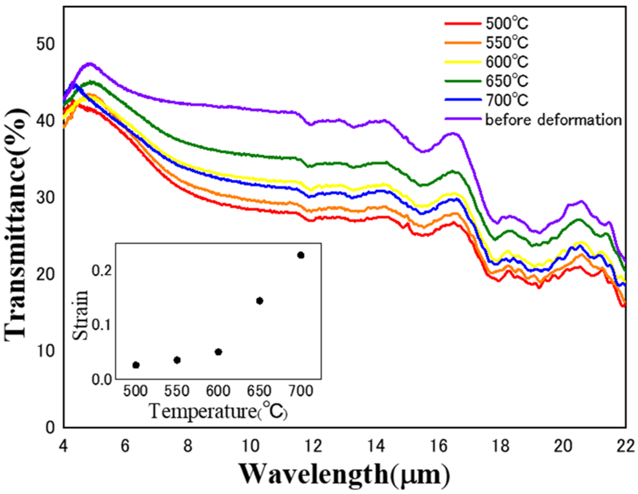

FIG. 3. Nominal strain measurement and FT-IR measurement of deformed Ge.

Figure 3 shows the infrared transmission spectra of the Ge single crystal after the low temperature deformation by direct electrical heating. The infrared transmittance of the sample with a thickness of 2 mm was measured by FT-IR. The nominal strain of the plastically deformed Ge sample under various temperatures was also plotted. The nominal strain was increased with an increase in temperature. The infrared transmittance was also increased with an increase in temperature when the deformation temperature ranged from 500 °C to 650 °C. However, it is noted that the transmittance of the deformed Ge sample at 700 °C was lower than that of the sample at 650 °C. Figure 4 shows SEM images of the lateral plane of the Ge sample deformed under various temperatures. In the case of the deformed sample at 500 °C, no apparent slip lines were observed, but aggregates of voids of several micrometers were observed [Fig. 4(a)]. On the other hand, dense slip lines were observed in the deformed sample at 650 °C; however, aggregates of voids were not observed [Fig. 4(b)]. In the deformed sample at 700 °C, many cracks were formed [Fig. 4(c)]. As mentioned before, the brittle–ductile transition of the Si and Ge single crystals depends on the dislocation velocity, namely, the temperature. Therefore, it is suggested that in the case of the low dislocation velocity at the low temperature of 500 °C, the brittle–ductile transition could not completely occur, leading to the generation of many voids on the lateral plane of the Ge sample. Such voids scattered infrared light and caused the decrease

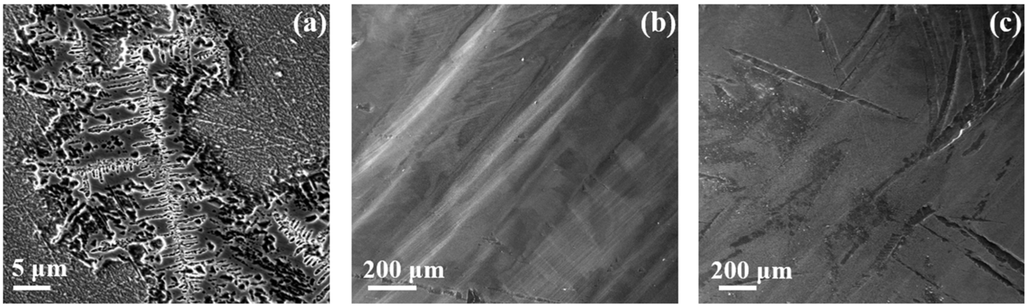

FIG. 4. SEM image of the side plane of Ge deformed at 500 °C (a), 650 °C (b), 700 °C (c).

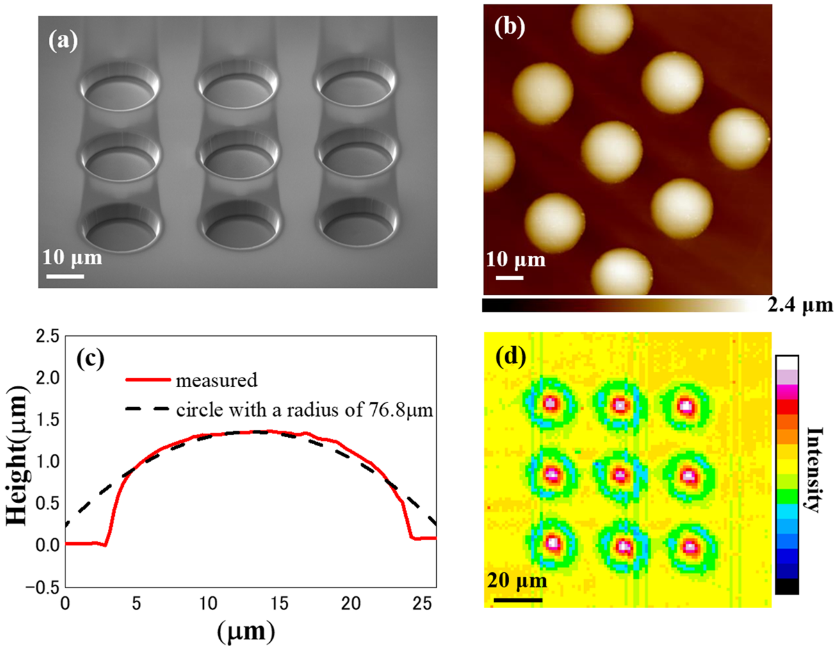

FIG. 5. (a) SEM image (tilt53°) of a Si mold fabricated by FIB, (b) AFM image of a Ge microlens array, (c) Ge microlens line profile, (d) infrared wavelength transmission microscope image of a Ge microlens array when focused at a position 25 μm away from the surface.

in transmittance. Since the generation of voids was suppressed as the deformation temperature was increased, the infrared transmittance was recovered in the range of 500–650 °C. Furthermore, it has been reported that the generated strain field around the dislocation in the crystal scatters light due to the photo elastic effect.[24,25] This suggests that a large slip band scatters infrared light in the case of the deformed Ge sample at 650 °C, even though no apparent voids or cracks were observed. In the case of 700 °C, the cracks due to the larger deformation reduced the infrared transmittance.[4] From these results, in our experiments, it is considered that the optimum temperature for the deformation of the Ge single crystal by direct electrical heating is 650 °C.

Figure 5(a) shows the SEM image of the mold of the Si single crystal tilted at 53°. The topographic image of the fabricated Ge microlens array is shown in Fig. 5(b). The line profile of the fabricated Ge microlens array is also shown in Fig. 5(c). The radius of curvature of the lens array was determined by fitting of the circular arc. The diameter of the microlens was 21.8 ± 0.5 μm, the height was 1.27 ± 0.6 μm, and the radius of curvature was 73.8 ± 6.6 μm. Since the refractive index of the Ge crystal in the infrared region is as high as about 4.0, the fabricated Ge microlens array can act as a plano-convex lens array and the focal length is calculated by the following equation:

$$f = \frac{R}{n-1}, \tag{1}$$

where f is the focal length, n is the refractive index, and R is the radius of curvature of the lens. The focal length of the fabricated Ge microlens array was designed to be 24.6 μm. We also confirmed the focused state of the infrared region ranging from 1 μm to 2 μm by using an infrared transmission microscope. The foci of the microlens array were observed in the plane 25 μm away from the front surface of the microlens array [Fig. 5(d)]. These results clearly indicated that the fabricated Ge microlens array can be used as a lens for the infrared region. The nominal strain of the Si mold after making Ge microlens array was 0.017. The cylinder pattern on the Si mold was not destroyed.

CONCLUSIONS

We confirmed that the temperature of the region with many dislocations in the Si single crystal was higher than that of the region with few dislocations during direct electrical heating. Since the electrical resistivity increased with an increase in number of dislocations, the drift electrons were scattered by the dislocations, leading to a temperature that was locally hot. It is considered that such hot spots enable low temperature deformation of the semiconductor single crystal by direct electrical heating. It was confirmed that Ge deformed at 650 °C had the highest infrared transmittance among the deformed Ge. From this fact, it was considered that the optimum temperature for the deformation of the Ge single crystal by direct electrical heating was 650 °C. We have also demonstrated the fabrication of the Ge microlens array with a focal length of about 25 μm by using a Si single crystal mold. The conditions of uniaxial pressing with direct electrical heating were a temperature of 650 °C, uniaxial pressure of 70.7 MPa, and processing time of 10 min. Such plastic deformation of semiconductor single crystals under lower temperatures will open the door to nanoimprinting technology for fabricating micro-optical devices.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] K. Nakajima, K. Fujiwara, W. Pan, and H. Okuda, Nat. Mater. **4**, 47 (2005).

[2] K. Morishita, K. Nakajima, T. Fujii, and M. Shiinoki, Appl. Phys. Express **4**, 106501 (2011).

[3] Y. Oshima, A. Nakamura, and K. Matsunaga, Science **360**, 772 (2018).

[4] K. Miura, Y. Shimotsuma, M. Sakakura, S. Gunji, T. Sakamoto, K. Morishita, and S. Hachinohe, Mater. Tehnol. **51**, 493 (2017).

[5] W.-D. Cao, X.-P. Lu, A. F. Sprecher, and H. Conrad, Mater. Sci. Eng. **129**, 157 (1990).

[6] W. A. Salandro, J. J. Jones, T. A. Mcneal, J. T. Roth, S. Hong, and M. T. Smith, J. Manuf. Sci. Eng. **132**, 051016 (2010).

[7] S.-W. Nam, H.-S. Chung, Y. C. Lo, L. Qi, J. Li, Y. Lu, A. T. C. Johnson, Y. Jung, P. Nukala, and R. Agarwal, Science **336**, 1561 (2012).

[8] Y. Yao, A. J. Hoffman, and C. F. Gmachl, Nat. Photonics **6**, 432 (2012).

[9] H. Ma, X. Zhang, Z. Zhang, Y. Wang, G. Wang, F. Liu, R. Cui, C. Huang, M. Wang, Y. Wei, K. Jiang, L. Pan, and K. Liu, J. Mater. Chem. C **7**, 12095 (2019).

[10] A. D. Stiff-Roberts, J. Nanophotonics **3**, 031607 (2009).

[11] H. Xiong and Z. Wang, J. Micromech. Microeng. **29**, 085002 (2019).

[12] V. S. Shiryaev and M. F. Churbanov, J. Non-Cryst. Solids **475**, 1 (2017).

[13] H. G. Dantanarayana, N. Abdel-Moneim, Z. Tang, L. Sojka, S. Sujecki, D. Furniss, A. B. Seddon, I. Kubat, O. Bang, and T. M. Benson, Opt. Mater. Express **4**, 1444 (2014).

[14] M. N. Polyanskiy, "Refractive index database," https://refractiveindex.info; accessed December 10, 2019.

[15] R. Yamazaki, A. Obana, and M. Kimata, Electron. Commun. Jpn. **96**, 42 (2013).

[16] G. L. Pearson, W. T. Read, Jr., and F. J. Morin, Phys. Rev. **93**, 666 (1954).

[17] W. T. Read, Jr., London, Edinburgh Dublin Philos. Mag. J. Sci. **46**, 111 (1954).

[18] R. H. Glaenzert and A. G. Jordan, Solid. State. Electron. **12**, 259 (1968).

[19] D. L. Dexter and F. Seitz, Phys. Rev. **86**, 964 (1952).

[20] D. Jena and U. K. Mishra, Appl. Phys. Lett. **80**, 64 (2002).

[21] W. G. Johnston and J. J. Gilman, J. Appl. Phys. **30**, 129 (1959).

[22] C. St. John, Philos. Mag. **32**, 1193 (1975).

[23] F. C. Serbena and S. G. Roberts, Acta Metall. Mater. **42**, 2505 (1994).

[24] K. Moriya, Philos. Mag. B **64**, 425 (1991).

[25] V. Monier, L. Capello, O. Kononchuk, and B. Pichaud, J. Appl. Phys. **108**, 093525 (2010).