

Shape control of nickel silicide nanocrystals on stress-modified surface†

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Regularly distributed dislocation networks with a controllable spacing have been formed by wafer bonding. Different kinds of Si bicrystals were fabricated by (001), (111) and (110) Si wafers bonded with (001) silicon-on-insulator (SOI). NiSi₂ formed on the bicrystal was found to be affected by the underlying dislocation arrays, confined by the dislocation grids while the surface stress and dislocation density is high enough. It has been demonstrated that through controlling the surface stress arrangement, the shape of the silicide nanostructures can be controlled and various nanostructures can be obtained. This study supports the fundamental understanding of the stress effect on the formation of silicide nanostructures on Si bicrystals and the shape-controlled nano-silicide could be useful for the growth of catalyst-assisted one-dimensional nanostructures.

Introduction

Surface physics at the nano-scale has attracted much attention due to novel properties and potential applications.^{1–5} The surface arrangement of nanostructures is not only an important issue for the discovery of the unique properties of a material, but also has led to profound understanding in modern physics. Quasi-two-dimensional silicide nanodot arrays were fabricated by surface steps on the surface of the strained Si on Si-Ge.⁶ On the other hand, surface stress is an approach to achieve arrangement control. The characteristics of dislocations in these materials have been extensively investigated.^{7–9} Silicon bicrystals have been a model substrate for surface control and dynamic reaction study with high regularity, several tens of nanometers below the surface and controllable dislocation spacings.¹⁰ There have been studies on the fabrication and fundamentals of silicon bicrystals.^{11–14} These

buried-screw dislocation arrays provide positive and negative surface stress contours on the edge of the grid and stress balance region close to the center.¹⁵ It has been realized that the surface stress would be intensively increased with shorter distance to the dislocation arrays and the edge of the contour provided the energetically favorable sites on the surface. However, only two-dimensional dislocation arrays were fabricated while other patterns have not been achieved. Meanwhile, with the advancement in nanoelectronics, the potential applications of nanosilicides and semiconductor/silicide nanoheterostructures have received increasing attention.^{16–19} The researches on the formation and reaction of nano-scaled silicide have been thoroughly investigated to improve the controllability and the stability of the heterostructure interface. Furthermore, the morphology and shape control are also the key parameters of the nanosilicides for catalytic chemistry, nanodevice and nanoscience. In this paper, we report the design and formation of bicrystals with different Si substrates and the effect of the dislocation array on the shapes of the nickel silicide formed on the surface. One-dimensional dislocation networks were formed at the interfaces in (111) or (110) Si bonded with (001) silicon-on-insulator (SOI). On the other hand, two-dimensional dislocation networks were formed by (001) Si wafer bonded with (001) SOI. NiSi₂ formed on the bicrystals surface was found to be affected by the underlying dislocation arrays.

Experimental

The silicon bicrystal was fabricated *via* silicon wafer bonding of a (001), (110) or (111) silicon wafer and a (001) SOI wafer with a 30 nm-thick top silicon layer. The silicon and SOI substrates were chemically cleaned using a standard RCA process followed by dilute HF dipping to produce clean and hydrophobic silicon surfaces. The wafers were cut along the <220> directions. Thus, the crystallography indication can be realized by the sample edges. The bonding angles were controlled by the difference between these edges. Once the

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angles were determined, they were placed face to face and a repulsive force was between the surfaces. The opposable surfaces were pushed to force them to contact. The wafers were bonded at room temperature at a specific twist angle and annealed at 1100 °C for 1 h. The backside silicon substrate of the SOI wafer was removed by mechanical grinding and chemical etching. The silicon oxide was then removed with dilute HF etching. After the HF dipping, the Si bicrystal was achieved, comprising a blank Si and a thin Si membrane with a dislocation array between. 1 nm-thick Ni thin film was deposited on the bicrystal substrates in an electron beam evaporation system with a base pressure higher than 1×10^{-6} Torr. The samples were then treated by rapid thermal annealing (RTA) at 600 °C for 5 min. High purity N₂ was flown during the RTA process. The quality of the bicrystals and the as-formed products were examined in a JEOL-2010 transmission electron microscope (TEM). The TEM samples were thinned down from the back side by mechanical grinding and polishing to ~100 nm thickness, then attached and transferred to the TEM sample holder for inspection. The distance between the surface and the dislocation plane was examined to be 25 nm.

Results and discussion

By wafer bonding of (001) Si and (001) SOI wafers with controlled misorientation angles, bicrystals with dislocation spacings from 2 to 80 nm were prepared. The misorientation between two sets of $\langle 2\bar{2}0 \rangle$ contributes to the formation of orthogonal arrays of screw dislocations. The cross grids with interspacings of 2, 20, 50 and 80 nm are shown in Fig. 1(a), (b), (c) and (d), respectively.

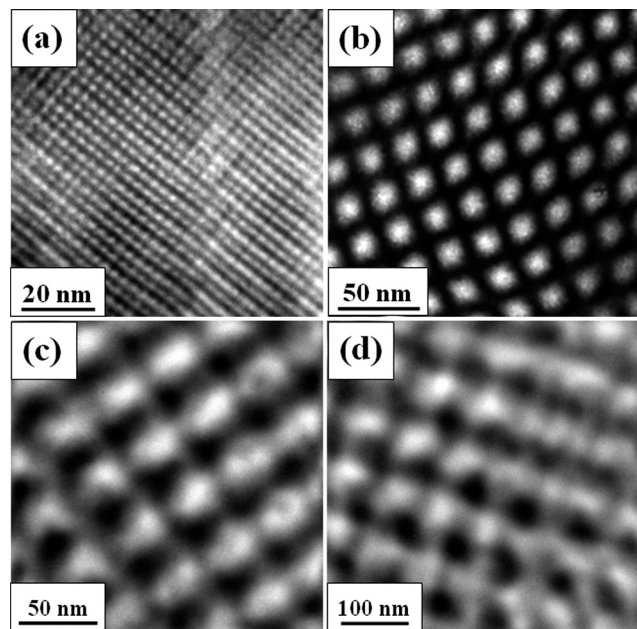


Fig. 1 TEM images of as-prepared (001)Si/(001)SOI bicrystal samples with (a) 2 nm, (b) 20 nm, (c) 50 nm and (d) 80 nm interspacings.

Without miscut dislocation interference, the dislocation arrays are well aligned. The interference by tilting dislocation was observed in Fig. 1(a). For the bonding of the (111) Si substrate with (001) SOI, one-dimensional (1D) dislocation arrays were formed. When the misorientation between one of the $\langle 2\bar{2}0 \rangle$ sets of (001) SOI and (111) Si substrate is small but the inclined angles of the others are near 30°, the dislocation array will become 1D, as shown in Fig. 2(a). The interspacing of the one-dimensional network is 10 nm. Fig. 2(b) is the corresponding diffraction pattern of Fig. 2(a). The result indicates that the dislocation lines are nearly parallel to $\langle 2\bar{2}0 \rangle$ directions with a small misorientation angle. The 1D dislocation array can also be obtained by (001) SOI and (110) Si wafer bonding. In Fig. 2(c) and (d), the dislocations are parallel to the $[2\bar{2}0]$ direction. But in Fig. 2(e) and (f), the dislocations are aligned in the $[400]$ direction. With control of the inclined angle between each $\langle 2\bar{2}0 \rangle$ and $\langle 400 \rangle$ set of the (001) and $\langle 2\bar{2}0 \rangle$ and $\langle 004 \rangle$ set of the (110) Si substrates,

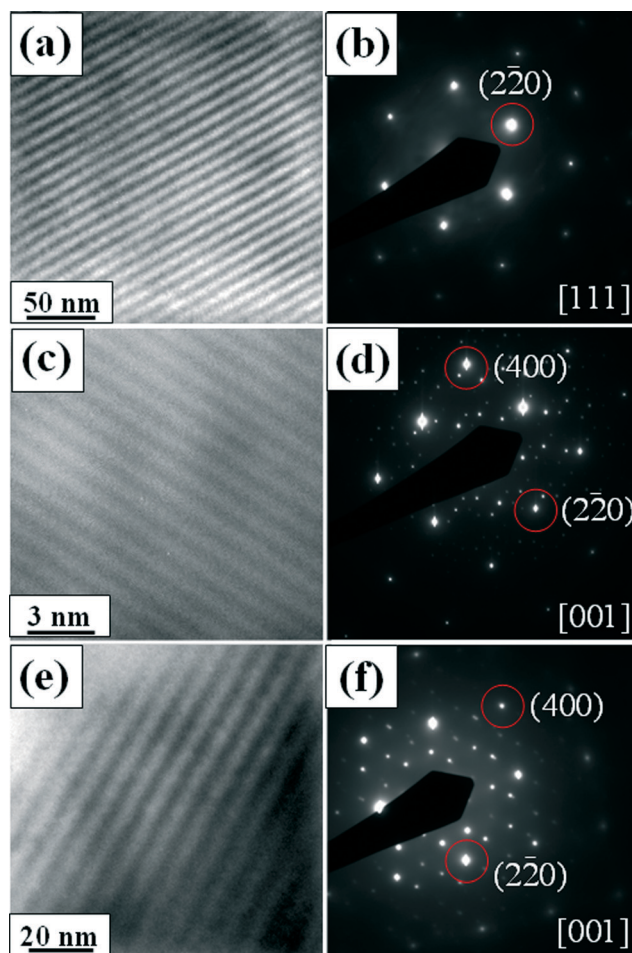


Fig. 2 TEM images of Si bicrystals with one-dimensional arrays. (a) $[2\bar{2}0](111)[\bar{2}20](001)$ sample with 10 nm interspacing, (b) corresponding diffraction pattern of (a). (c) $[2\bar{2}0](110)[\bar{2}20](001)$ sample with 1 nm interspacing, (d) corresponding diffraction pattern of (c). (e) $[004](110)[\bar{4}00](001)$ sample with 6 nm interspacing, (f) corresponding diffraction pattern of (e).

the dislocation array will be parallel to $\langle 2\bar{2}0 \rangle$ and $\langle 400 \rangle$ directions, respectively. Fig. 2(c) and (e) show the 1D dislocation array with 1 nm and 6 nm interspacings, respectively. Fig. 2(d) and (f) show the corresponding electron diffraction patterns of Fig. 2(c) and (e), respectively.

The NiSi_2 nanostructures formed on the blank Si are shown in Fig. 3(a). The nanoclusters are rounded. The inset shows the selected area electron diffraction pattern, which indicates the phase of the silicide nanodot was NiSi_2 . On the other hand, the nickel silicide nanoclusters formed on the surface of the bicrystal was affected by the underlying dislocation arrays. As shown in Fig. 3(b), the nanoclusters are square or rectangular in shape and confined by the dislocation grids. Low-magnification TEM images demonstrated that the as-formed silicides were mostly square or rectangular, affected by the underlying dislocation arrays (ESI† Fig. S1). Silicide nanoclusters were formed on the bicrystal with a 3.1 nm interspacing. The selected area electron diffraction pattern in Fig. 3(c) of the silicide nanocluster in Fig. 3(b) identified the NiSi_2 phase and the crystallinity, which was due to the small (0.46%) lattice mismatch of the crystal structure of the NiSi_2 and Si. The presence of the $\{200\}$ diffraction patterns is evidence of the NiSi_2 phase because they will not appear in a Si diffraction pattern. We have performed XRD to highlight the data between 56.05 – 56.45° (ESI† Fig. S2). The peak intensity is not strong but auxiliary to demonstrate the NiSi_2 phase.

For nickel silicide nanoclusters formed on the bicrystals with a relatively large interspacing, the shape confinement was less evident. The edges of silicide nanoclusters formed on the bicrystals with 15, 20 and 50 nm interspacings are not well-aligned with the dislocation grids, as seen in Fig. 3(d), (e) and (f), respectively. From these experimental results, the shape confinement effect becomes less pronounced and the influence of the underlying dislocation networks is weakened with the increasing dislocation interspacing.

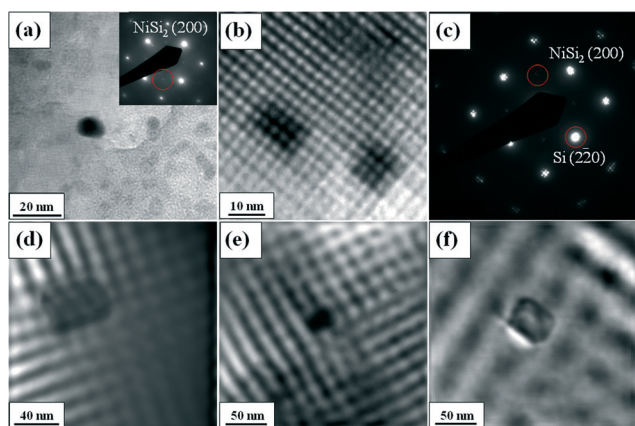


Fig. 3 TEM images of NiSi_2 grown on (a) blank Si and bicrystals with (b) 3.1 nm, (d) 15 nm, (e) 20 nm and (f) 50 nm interspacings, (c) corresponding diffraction pattern of (b). Inset in (a) shows the selected area electron diffraction pattern.

On the other hand, relatively long silicide nanorods were formed on the 1D dislocation arrays. Fig. 4 shows silicide nanorods formed on the one-dimensional dislocation array with a 10 nm interspacing and the inset in each figure displays the schematic illustration. Silicide nanorods formed on the bicrystals are confined by the parallel dislocation lines. The widths of the nanorods ranged from 10–50 nm and the lengths of the nanorods were from 63–225 nm. The width of the nanorods was the integer of the grid spacing but the length of the nanorods was not affected by the network; thus, the products would grow longer. The aspect ratios of the nanorods were measured to be 2.5–4.5. Based on the TEM observation, at the ends of nanorods without dislocation confinements, uneven edges were also observed. This indicates that substrates with 1D dislocation arrays are more favorable for the growth of silicide nanowires.

The Si bicrystal has been investigated by atomic force microscopy (AFM) which revealed that there were no regular surface steps and the roughness is ~ 0.055 nm (rms) due to the quality of the SOI wafer. The results also confirmed that the surface of the bicrystal was as flat as commercial Si substrate and the geometry of the nanosilicide was purely attributed to the surface stress. On the other hand, self-ordering of nanostructures at crystal surfaces has been investigated with time-resolved STM to show that the strain-mediated interaction among surface defects on the strained film is responsible for the formation mechanism.²⁰ The confinement effect of dislocation arrays on the surface nanoclusters in the bicrystal samples have provided an influential factor of the surface tension by different bonding twist angles. They

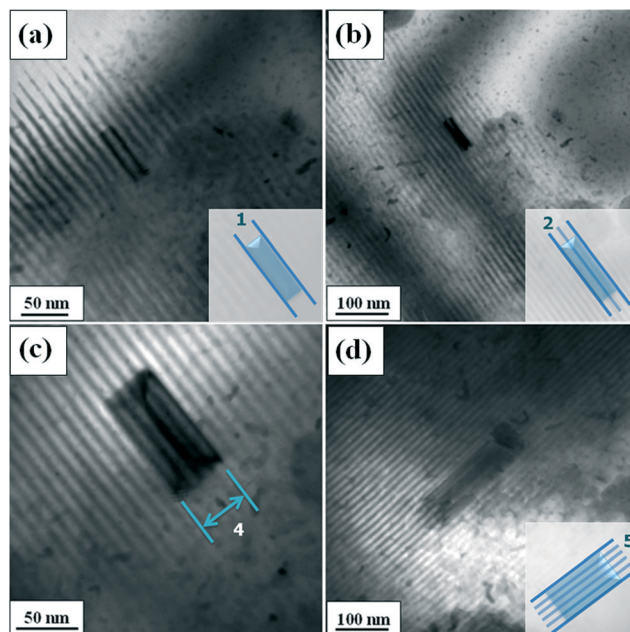


Fig. 4 TEM images of NiSi_2 silicide formed on bicrystals with 10 nm one-dimensional interspacing. The widths of the nanorods are (a) 10 nm, (b) 20 nm, (c) 40 nm and (d) 50 nm. Insets show the schematic illustrations.

indicated that the larger the twist angle is, *i.e.*, the smaller interspacing, the higher the surface energy is. The present study shows that the confinement effect is more significant in Si bicrystals with smaller dislocation spacing even when the dislocation spacing is much shorter than the distance from the surface to the dislocation plane. It means that the higher the surface energy, the stronger the influence on the growth of nanoclusters on the surface of bicrystals, as a result of small dislocation interspacing and high energy at the bonding interface of two single crystalline Si. According to the theoretical calculation, the distance from the surface to the dislocation plane has great influence on the surface strain, *i.e.*, the shorter the distance is, the larger the surface strain persisting on the surface. At the same interspacing of the dislocation grids, there is more strain energy at the surface with a shorter distance from the surface to the dislocation plane. These factors predict that the shape confinement should be more significant at a shorter distance.¹⁵ Therefore, additional control may be conducted by the variation of the distance from the dislocation plane to the surface. The observation of the stress confinement of the growth of nanostructures is potentially significant for fundamental understanding and applications in nanotechnology and surface physics.

Conclusions

In summary, we have fabricated different kinds of Si bicrystals by bonding of (001), (111) or (110) Si wafers with (001) SOI wafers. One-dimensional dislocation arrays were formed in bicrystals by bonding of (111) or (110) Si wafers with (001) SOI wafers while two-dimensional dislocation networks were formed by wafer bonding of (001) Si and (001) SOI wafers. The shapes of nickel silicide nanoclusters formed on the bicrystals were found to be affected by the underlying dislocation arrays. Square and rectangular silicide nanoclusters were formed on two-dimensional dislocation grids with a small spacing. For dislocation spacing larger than 15 nm, the confinement effect is less pronounced. For the one-dimensional dislocation arrays with a 10 nm spacing, the confinement effect is evident. With a higher aspect ratio, substrates with 1D dislocation arrays are more favorable for the growth of silicide nanowires. The results are consistent with the theoretical prediction that the higher the surface strain energy, the stronger the influence on the growth of nanoclusters on the surface of bicrystals. This study supports the fundamental understanding of the stress effect on the formation of the silicide nanostructures on Si bicrystals and the shape-controlled nanosilicide could be useful for the growth of catalyst-assisted one-dimensional nanostructures.

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