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Orientation-controlled nucleation of crystal silicon grains in amorphous silicon on a rolled nickel tape substrate

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Crystal silicon grains with grain sizes in excess of 10 μm and orientation control over all three directions were produced by depositing an amorphous silicon thin film on a cold-rolled and annealed nickel tape and annealing at 600 °C for 2 h. The needle-like morphology of the grains indicated that the crystallization was mediated by $NiSi_2$. All grains had their [110] axis about 21° off the surface normal. Furthermore, nearly all of them had the same rotation about the [110] axis except for presence of twins and/or type *A–B* formations. Despite the use of the nickel substrate, the Ni concentration within the Si film was below the detection limit of energy-dispersive x-ray spectroscopy (10^{19} cm^{-3}). This low-Ni contamination level is attributed to the presence of an oxide layer between the Ni substrate and the Si film. © *2001 American Institute of Physics.*
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Polycrystalline silicon (poly-Si) is gaining importance for thin-film transistor (TFT) applications since it has a higher carrier mobility and current carrying capacity than hydrogenated amorphous silicon (*a*-Si:H). Among the many different methods for producing poly-Si films, silicide-mediated crystallization (SMC) of amorphous silicon[1–4] offers the advantage of producing large-grained poly-Si films at temperatures low enough for glass substrates while maintaining a high throughput without the need for expensive machinery. Indeed, processing times as short as a few seconds[5] and channel mobility as high as 170 cm^2/V (Ref. 6) have been reported.

For applications, however, the location and orientation of grains need to be controlled as well as the grain size. These issues become more critical as grains become larger, since there are fewer grains within a channel. While there have been reports of controlling the location of grains,[7,8] very few results have been reported on controlling the orientation of grains beyond inducing a texture.[9] Note, however, that a poly-Si film with controlled grain orientation is tantamount to a single-crystalline Si film. Developing such a film could have an enormous impact that reaches beyond TFT applications, since it would enable TFT technology to fabricate high-performance devices that so far have been limited to Si wafers, and to integrate them with TFT-driven displays.

Controlling the grain orientation in poly-Si is difficult because nucleation is a stochastic process. However, if an external template for crystallization is provided, both the orientation and location of crystal grains can be controlled. In this letter, we report on results of using cold-rolled and annealed Ni tapes as such a template for crystallization of *a*-Si:H thin films. We find that crystallization is mediated by $NiSi_2$ formation, and that all Si grains have their [110] axis oriented the same way within a few degrees. Furthermore, the rotation of grains about the [110] axis was the same except for the presence of twins and/or type *A–B* formations. The concentration of Ni in the Si film, however, was below the detection limit of energy-dispersive x-ray spectroscopy (EDS) (10^{19} cm^{-3}) due to the presence of an interfacial oxide layer.

Commercial nickel tapes of 3 mm thickness were rolled at room temperature down to <100 μm and annealed at 900 °C for 4 h. Following the anneal, the tapes were polished to a mirror finish using a suspension of 0.3 μm Al_2O_3 in deionized water. Such a treatment is known to align the orientation of nickel grains to produce nearly single-crystalline Ni tapes[10] sufficient for growth of epitaxial growth of $YB_2Cu_3O_{7-x}$ films.[11] The Ni tapes used in this letter were analyzed using x-ray pole figure measurements, and were confirmed to be nearly single crystalline with the [001] tilted by $\sim 21°$ off the surface normal (not shown). A 100-nm-thick *a*-Si:H film was deposited on the Ni tapes using inductively coupled plasma of SiH_4. Prior to start of the deposition, the substrate was cleaned by exposure to Ar/H_2 plasma for 20 min. The base pressure, deposition pressure, deposition temperature, and the plasma power was 1×10^{-6} Torr, 8×10^{-3} Torr, 200 °C, and 800 W, respectively. After deposition, the samples were annealed in a high vacuum furnace at 600 °C for 2 h. Silicon samples for transmission electron microscopy (TEM) analysis were prepared by the lift-off process using HF and carbon-coated copper grids.

Figure 1 shows a dark-field plan-view TEM image of the annealed silicon film. Two needle-shaped, crystalline-Si grains can be observed. The inset shows the selected area diffraction (SAD) pattern from the indicated areas. Three points should be noted. First, the region outside the grains is fully amorphous. Second, not only is the grain very large with linear dimension in the excess of 10 μm, it is also essentially single crystalline with [110] orientation. Third, the orientation of the two grains are nearly identical, as can be seen by comparing the directions of the ''needles'' of the grains. The last two points are significant, since they imply that the two grains observed in Fig. 1 have nucleated in such a way that should they grow larger and merge, they should form a nearly single grain with only a low-angle grain boundary between them.

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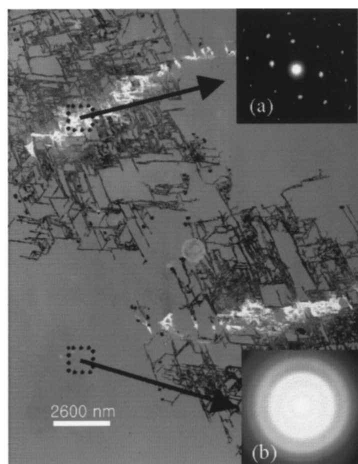

FIG. 1. TEM dark-field image of the Si film after a 2 h anneal at 600 °C. Inset shows the selected area diffraction pattern from the indicated areas.

In order to confirm the degree of control over the orientation of the grains, the SAD patterns of 20 randomly selected grains from a single, continuous Si film were analyzed. We found that all grains have [110] orientation. Furthermore, the rotation of the grains about their [110] axis was not random, as nearly all of them could be grouped into three distinct groups. Figure 2 shows the SAD patterns representative of each group (a)–(c), plus two grains that did not belong to any group (d) and (e). The crystalline volume fraction, estimated from the TEM images of the grains, was about 34%.

Figure 3 shows the distribution of the tilt angles of the [110] axis of the grains off the surface normal. We find that all the grains have, on the average, their [110] axis oriented 21° off the surface normal, similar to the [001] axis of the underlying Ni substrate. The distribution of the rotation angles of the grains about the [110] axis, arbitrarily defined

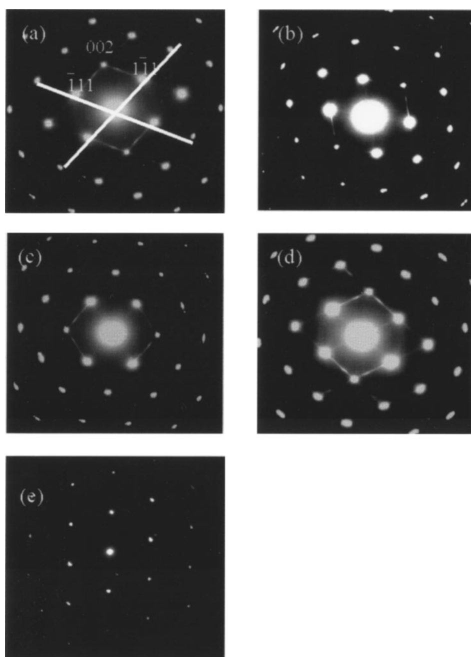

FIG. 2. Selected area diffraction patterns of three grains representative of three groups into which nearly all observed grains can be classified (a)–(c), and those of two grains which do not belong to any group (d) and (e).

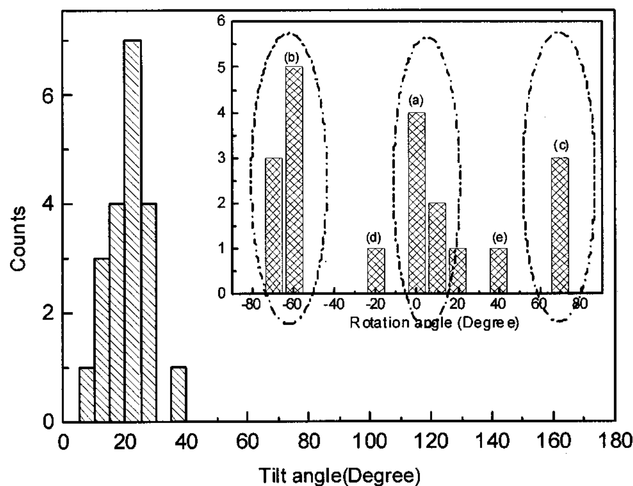

FIG. 3. Distribution of the tilt angles of the [110] axis of the grains off the surface normal. Inset shows the distribution of the rotation angles of the grains about the [110] axis, arbitrarily defined to be the angle between the [002] axis of the grain and the [002] axis of the grain shown in Fig. 2(a).

to be the angle between the [002] axis of the grain and the [002] axis of the grain shown in Fig. 2(a), is shown in the inset of Figure 3. We find one group, labeled (a) and corresponding to the SAD pattern shown in Fig. 2(a), centered around 0°. Two other groups, labeled (b) and (c) and corresponding to the SAD patterns shown in Figs. 2(b) and 2(c), respectively, are spaced about 70° on either side of (a). These values are not coincidental. Instead, (b) and (c) are the result of 180° rotations of Fig. 2(a) about the $[1\bar{1}1]$ and $[\bar{1}11]$ axes, respectively. A similar relationship exists between (d) and (e), as Fig. 2(e) is the result of a 180° rotation of Fig. 2(d) about the $[1\bar{1}1]$ axis.

The large grain sizes, the needle-like shape, and [110] orientation of grains bear a strong resemblance to Si grains that have been crystallized via $NiSi_2$.[4,12] During such a silicide-mediated crystallization, many randomly oriented Si grains nucleate easily, and grow along the [111] direction of the crystallized grains through migration of the $NiSi_2$ particles. However, if a grain has its [110] axis normal to the surface, as all grains studied here nearly do, it can grow to a large, needle-shaped grain because it has four [111] axes parallel to the Si film. Indeed, the angle between the needles seen in Fig. 1, when corrected for the projection angle, is 70.6°, in close agreement with the angle between the [111] axis of Si, which is 70.5°. Furthermore, many needles sport a dark lump at their tips, which presumably are $NiSi_2$ particles.

The source of Ni for SMC is obviously the Ni substrate. The observed control over the orientation of the nucleated Si crystals can then be attributed to the nearly single-crystalline nature of the Ni tapes. Initially, silicides can form only at the Si/Ni interface. However, because the Ni substrate is nearly single crystalline, the silicide particles that form at the Si/Ni interface should all have the same orientation in all three directions, as should the Si crystal grains which form due to migration of these silicide particles. The 70° difference between the rotation angles observed in Figs. 2(b)–2(e) can then be attributed to either twinning, or to the difference between type *A* and *B* SMC, in which the $NiSi_2$ particle is rotated 180° about the Si ⟨111⟩ axis. It should be mentioned

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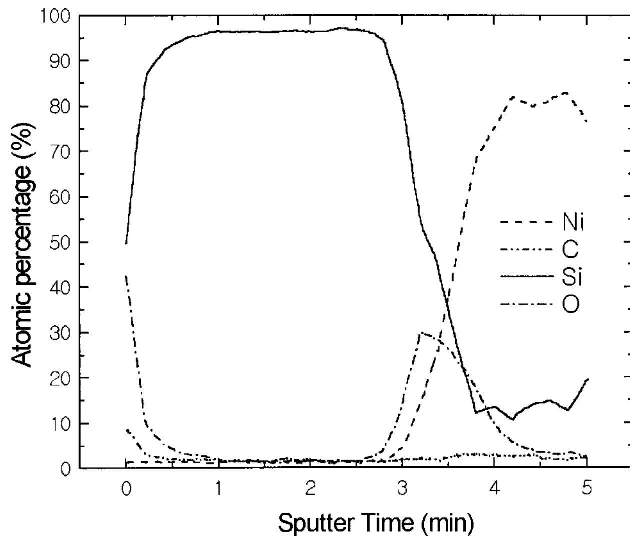

FIG. 4. AES depth profile spectrum of the annealed film. Note the strong peak at the Si/Ni interface, indicating the presence of an oxide layer.

here that the values of tilt and rotation angles have standards of deviation from the average that is much larger than that of the substrate. However, we note that the copper grid used for TEM sample preparation can easily be deformed during handling, and that this can lead to variation in the values of angles being measured.

What is not obvious, however, is why the entire Si layer should not transform into a silicide layer. $NiSi_2$ can form after anneals of only 325 °C,[1] and the supply of Ni is essentially infinite. However, the low grain density observed in Fig. 1 indicates that the supply of Ni was very limited. This was confirmed by the failure of EDS to detect any Ni in the partially crystallized film (not shown), indicating that the density of $NiSi_2$ particles in the film was very low.

The reason can be found in Fig. 4, which shows the Auger electron spectrum (AES) depth profile of an annealed film. Again, no Ni signal can be detected in the Si layer. However, a clear oxygen peak can be found at the Si/Ni interface, indicating that the plasma cleaning did not completely remove the oxide layer on the Ni substrate surface. At this point, it is not clear what kind of an oxide layer is present (NiO, SiO_2, or something in between). We note, however, that oxygen atoms in NiO become mobile above $\sim 300\,°C$,[13] and that annealing NiO above 600 °C in the presence of hydrogen can lead to reduction of NiO.[14] Furthermore, the heat of formation of SiO_2 is larger than that of any nickel silicides, oxides, and their mixtures by more than 100 kJ/mol, leading to formation of SiO_2 at the expense of them.[15] Therefore, we argue that it is very likely that the oxide layer contains SiO_2.

The presence of SiO_2 can significantly alter the reaction kinetics between Si and Ni, since SiO_2 is stable with respect to both of them, thus forming an effective diffusion barrier. Indeed, a SiO_2 layer that is only 2 nm thick is sufficient to inhibit a reaction between Si and Ni up to 700 °C.[15] Therefore, we attribute the low-density Si grains and $NiSi_2$ particles to the presence of the oxide layer that acts as a diffusion barrier. The fact that we do observe SMC, however, indicates that the oxide layer must have broken up at few random spots, either stochastically or due to pre-existing pin holes in the oxide layer, thus allowing silicide particles to form.

The entire crystallization process can then be described by the initial formation of $NiSi_2$ at the few random holes in the oxide followed by lateral epitaxial crystallization of the remaining *a*-Si film through migration of the $NiSi_2$ particles. Thus, we can envision that by intentionally forming a dense oxide layer and then etching holes in it to expose the Ni substrate prior to deposition of Si film, we can control *both the location and orientation* of the crystal grains that form. Furthermore, previous works have shown that SMC can also be initiated by simply pressing a Ni template upon an *a*-Si film and annealing at low temperature ($<600\,°C$).[7,8] Therefore, by using a nearly single-crystalline Ni tape which has raised bumps, it should be possible to produce large, orientation-controlled crystalline Si grains on glass in a manner compatible with the present TFT technology.

In conclusion, we have nucleated orientation-controlled Si grains in *a*-Si film using a cold-rolled, annealed Ni tape as the substrate. The crystallization proceeds via migration of $NiSi_2$ particles, resulting in large grains in an epitaxial relationship with the underlying Ni substrate. The level of Ni contamination in the film was below $10^{19}\ cm^{-3}$ due to the presence of an interfacial oxide layer that limited reaction between Si and Ni.

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