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Promoted Growth of Bi Single-Crystalline Nanowires by Sidewall-Induced Compressive Stress in On-Film Formation of Nanowires

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RESEARCH ARTICLE

To increase the density of Bi nanowires grown by our unique on-film formation of nanowires (OFF–ON) method, we introduced a technique for enhancing compressive stress, which is the driving force for the nanowire growth. The compressive stress could be controlled by modifying the substrate structure. A combination of photolithography and a reactive ion etching technique was used to fabricate patterns on a thermally oxidized Si(100) substrate. It was found that the density of Bi nanowires grown from Bi films in 100×100 μm^2-sized SiO_2 patterns increases by a factor of seven over that from non-patterned substrates. Our results indicate that the density of Bi nanowires can be increased by enhanced compressive stress arising from a sidewall effect in the optimized pattern size and array.

Keywords: Compressive Stress, Bi Nanowires, Sidewall, On-Film Formation of Nanowires.

1. INTRODUCTION

Bismuth (Bi) is an intrinsic semimetal with intriguing properties such as a highly anisotropic Fermi surface, a low carrier concentration ($n \approx p \approx 3 \times 10^{17}$ cm^{-3}), and a small effective mass ($\sim$0.001 m_o) and a long mean free path ($\sim$1.35 μm) of carriers. For this reason, transport properties have been investigated on a variety of Bi-based structures.[1–3] In particular, Bi nanowires have attracted the large interest in a research stream, seeking novel quantum phenomena such as wire-boundary scattering effects, quantum confinement effects, and the semimetal-to-semiconductor transition. Furthermore, interest in the one-dimensional (1D) Bi structures has been reignited since a few research groups[4–7] predicted that Bi nanowires should have a thermoelectric figure-of-merit (ZT) far higher than that of bulk Bi.

High quality single-crystalline Bi nanowires are required to investigate those properties in depth. Several methods including a pressure injection technique, electroplating using anodic alumina oxide (AAO) templates, and a vapor–liquid–solid (VLS) method using catalysts, have been widely used for nanowire growth.[8–10] However, Bi nanowires grown by these methods were often polycrystalline, and require subtle post-growth processing such as the removal of catalysts and templates. Previously, we developed a method to grow single-crystalline Bi nanowires without the aid of catalysts and templates, which we referred to as the on-film formation of nanowires (OFF–ON) method.[11–12] The OFF–ON is a stress-induced nanowire growth technique activated by a thermodynamic driving force that is provided by compressive stress accumulated in a film. This compressive stress arises from the difference in thermal expansion between the film and the substrate. The high quality nanowires grown by the OFF–ON may also serve as a good 1D test-bed to study fundamental physics of emerging topological insulators since they are wholly single-crystalline and their surfaces are smooth, protecting potential surface topological insulator phases more robustly with no defect states in the band gap.[13–14]

The density of Bi nanowires grown by the OFF–ON method, however, appeared to be lower than densities reported using other growth methods.[8–10, 15] This was regarded as a major drawback of this method. Furthermore, localization of growth sites was difficult using the OFF–ON method. In this study, SiO_2 sidewalls patterned on a SiO_2/Si substrate were used to increase the Bi nanowire density. We confirmed that the density of Bi nanowires was significantly increased from Bi thin films surrounded by SiO_2 sidewalls, and demonstrated that the pattern size should be properly optimized to obtain high density Bi nanowires. This pattern-size-dependent increase

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in Bi nanowire density is discussed in relation to compressive stress enhancement caused by the SiO_2 sidewall.

2. EXPERIMENTAL DETAILS

Figure 1(a) schematically shows the conventional OFF–ON process, illustrating the origin and driving force for the spontaneous growth of Bi nanowires. A Bi thin film is initially deposited onto a SiO_2/Si substrate by ultrahigh vacuum (UHV) radio frequency (RF) sputtering. Annealing the Bi thin film at a temperature near its melting point, thermal expansion mismatch between the Bi film and the substrate generates compressive stress acting in plane. Bi nanowires randomly grow to relieve this compressive stress via atomic diffusion. No patterning steps are used in the conventional process.

In contrast, SiO_2 sidewall fabrication is introduced just before the OFF–ON process in this work. Figure 1(b) shows step-by-step schematics of the sidewall fabrication using photolithography, followed by the OFF–ON. First, photo-resist (PR) patterns are developed with different size and regularity, all square in shape: 10×10 μm^2, 100×100 μm^2 (type-A), 100×100 μm^2 (type-B), 1000×1000 μm^2. The SiO_2 layer is selectively etched by CF_4 reactive ion etching (RIE), using the PR patterns as etch barriers. In this study, the etch depth was fixed at 100 nm, which corresponds to one third of the total SiO_2 thickness (300 nm). Bi films are subsequently deposited on this substrate, where SiO_2 was etched off on non-PR-protected areas but remains intact under PR patterns. Next, a lift-off process leaves behind Bi film patterns enclosed by SiO_2 sidewalls. The OFF–ON method is then applied to grow high quality single-crystalline Bi nanowires on this patterned Bi film. In this case, the Bi nanowire growth is localized because it only occurs on Bi films separated by SiO_2 sidewalls.

Optical microscopy (OM) was used to make accurate measurements on Bi nanowire density. Fifty pattern sites per sample were randomly selected for samples with pattern sizes of 10×10 μm^2, 100×100 μm^2 (type-A), and 100×100 μm^2 (type-B), while three areas were chosen for 1000×1000 μm^2-sized patterns. An average number of nanowires were calculated per pattern area and the number was multiplied by the ratio of the pattern area to the area of interest. In this work, the standard area was chosen at 2.25 cm^2, which is the area of a non-patterned reference sample, leading to the nanowire density in unit of counts/2.25 cm^2. A reference sample (non-patterned sample) containing Bi nanowires grown under the same conditions as for patterned samples was prepared for comparison with its patterned counterparts, and 150 sites were randomly selected to measure the Bi nanowire density.

3. RESULTS AND DISCUSSION

Figure 2(a) shows representative OM images of SiO_2 patterns before Bi film deposition. It is seen from the figure that all patterns are perfect squares in shape and two types of 100×100 μm^2 pattern arrays are apparent; one in which patterns are perfectly separated from each other (type-A) and another where patterns make contact with each other at corners (type-B). Bi films reproduce these

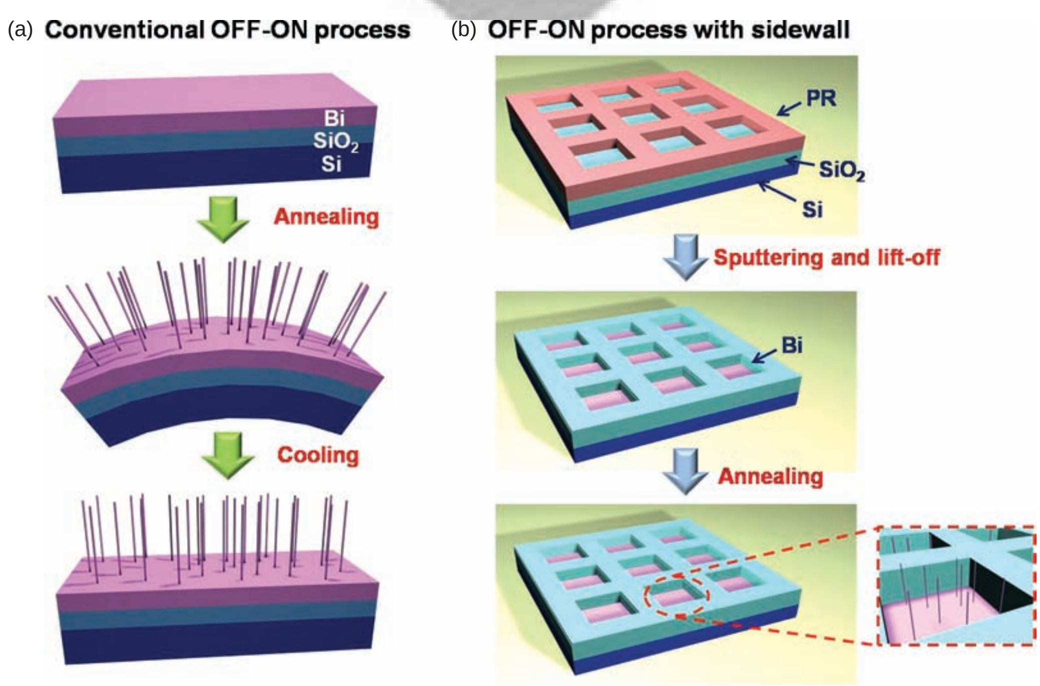

Fig. 1. Schematic pictures showing Bi nanowire growth by (a) the conventional on-film formation of nanowires (OFF–ON) process and (b) the OFF–ON process assisted by sidewalls.

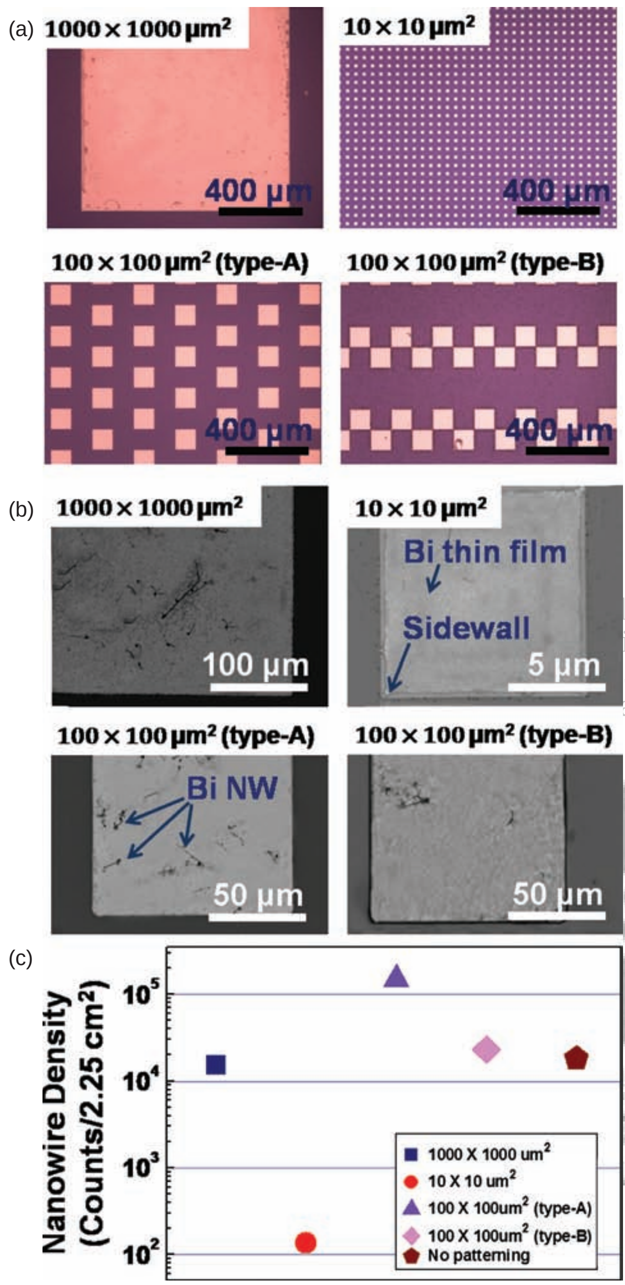

Fig. 2. (a) Optical microscopy (OM) images of SiO_2 patterns with different pattern sizes and arrays, (b) OM images of nanowires grown on Bi films enclosed by the SiO2 sidewall patterns, (c) Bi nanowire density depending on the pattern size and array. A non-patterned reference sample is also shown for comparison.

SiO_2 patterns since the films deposited over areas other than inside the square trenches surrounded by the SiO_2 sidewall are removed during the lift-off process.

The representative OM images of nanowires grown on Bi films in the four SiO_2 sidewall patterns are shown in Figure 2(b). More nanowires are seen to be grown on a 100×100 μm^2—sized pattern (type-A) while almost no nanowires are observed on a 10×10 μm^2 pattern. Figure 2(c) shows Bi nanowire densities for patterned samples and a reference sample (non-patterned SiO_2/Si substrate). It is found that the nanowire density on 1000×1000 μm^2—sized patterns is the almost same as that of the reference sample, while it decreases by about two orders of magnitude for 10×10 μm^2—sized patterns The decrease in nanowire density observed on the 10×10 μm^2—sized patterns suggests that the amount of Bi confined in the small trenches is not sufficient to support Bi nanowire growth. In addition, a complicated stress state caused by spatially varying excessive compressive stress induced by sidewalls may hinder uniform compressive stress evolution over the film, which is recognized as a driving force for nanowire growth by the OFF–ON method. For the 1000×1000 μm^2—sized patterns, the compressive stress induced by sidewalls is most likely attenuated inside the patterned Bi films, resulting in almost no change in nanowire density as compared to the reference sample.

In contrast, the Bi nanowire density on 100×100 μm^2—sized patterns (type-A) is significantly increased by a factor of 7 over the reference sample. This is attributed to the sizable enhancement of quasi-uniform compressive stress induced by sidewalls. Interestingly, the other type of 100×100 μm^2—sized patterns (type-B) has a nanowire density very similar to that of the reference sample, even though the pattern size of type-B is exactly the same as that of type-A. This difference arises from different manners of arraying the patterns. Unlike type-A consisting of perfectly encaged patterns, patterns in type-B share two corners with adjacent patterns, which may function as stress-relieving channels. Therefore, the existence of perfect sidewalls that can cage an induced compressive stress is considered to be the primary reason why type-A and type-B patterns yield such different nanowire densities.

In order to investigate this sidewall effect in more detail, further study was performed. Figure 3 shows tilted scanning electron microscopy (SEM) images of 100×100 μm^2—sized patterns (type-A) with (Fig. 3(a)) and without (Fig. 3(b)) sidewalls. We tilted the samples about 60° away from the substrate normal to show both pattern array and nanowire distribution, resulting in ribbon-like elongated pattern images (see the insets of Fig. 3 for better understanding). From the figure, it is clear that Bi nanowires are grown only on the black ribbon-like Bi pattern areas that correspond to the pink squares in insets. More importantly, the density of Bi nanowires is larger on the patterns with sidewalls than on the same-sized patterns without sidewalls, reflecting that nanowire growth is facilitated by the sidewalls. This increases in the nanowire density most likely results from the reinforced compressive stress provided by the sidewalls, which functions as both stress generators and stress reservoirs.

The sidewall effect manifests a thermodynamic driving force of the OFF–ON method, employed in this study to grow Bi nanowires. To reiterate, the compressive stress

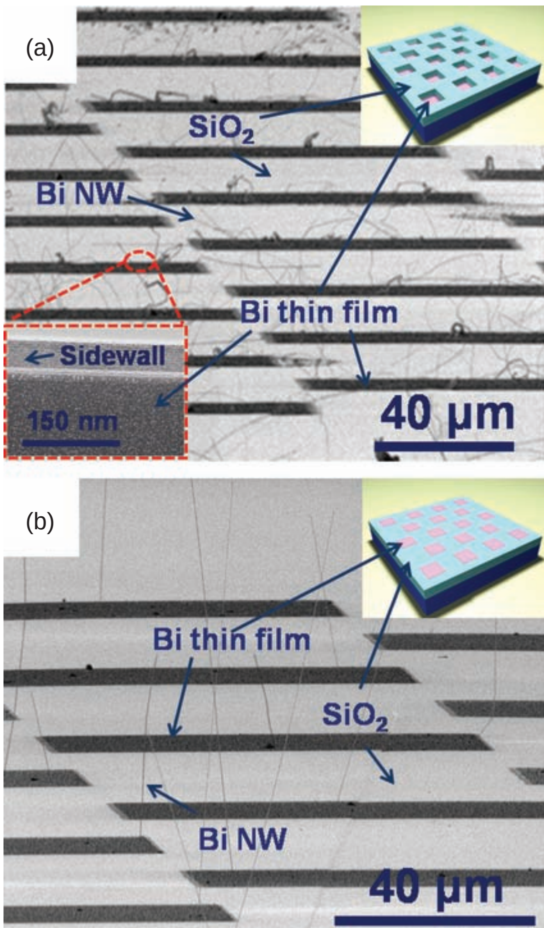

Fig. 3. Scanning electron microscopy (SEM) images of Bi nanowires grown on 100×100 μm^2-sized Bi patterns (a) with sidewalls and (b) without sidewalls.

caused by the thermal expansion mismatch between the Bi film and the substrate is known to be the driving force for nanowire growth by the OFF–ON method. Bi film with a high thermal expansion coefficient (13.4×10^{-6}/°C) expands during annealing at 260–270 °C (estimated surface temperature: 250–260 °C), while the SiO_2/Si substrate with a low thermal expansion coefficient ((0.5×10^{-6}/°C)/(2.4×10^{-6}/°C)) restricts the expansion of the film, putting the Bi film under an in-plane compressive stress. Bi nanowires spontaneously grow to relieve this compressive stress, by diffusion of Bi atoms. If this mechanism is a real case, the Bi nanowire growth should be promoted by the compressive stress reinforcement provided by sidewalls. Indeed, the results of Figures 2 and 3 demonstrate that the enhancement in compressive stress due to the presence of sidewalls leads to the promotion of Bi nanowire growth. However, the compressive stress additionally induced by sidewalls is dependent on pattern size, as shown in Figure 2.

We calculated the pattern size-dependent compressive stress profiles using a simplified film stress equation in relation to the extended Stoney's formula, which has been extensively used to understand stress distributions over different film profiles.[16–17] The stress (σ) that a thin film on the substrate feels can be expressed in a simple form

$$\sigma = \left(\frac{x}{h_{\text{film}}}\right) \exp\left[-C\left(\frac{x}{h_{\text{film}}}\right)\right] \tag{1}$$

where h_{film} is the film thickness, x is the distance from the film edge, and C is a constant characteristic of stress state, particularly related to film edge. Applying the extended Stoney's formula, the stress constant C can be replaced by

$$C = \frac{E_s}{6(1-v_s^2)}\left\{-\frac{1}{2}[(1-3v_s)h_s^2\left[1+\frac{h_s - h_{\text{wall}}}{2h_s}\right.\right.$$
$$\left.\left.[5 - v_s - (1-v_s)L_{\text{in}}]\right]\right\} \tag{2}$$

where E_s, ν_s, and h_s are the Young's modulus, Poisson's ratio, and height of the substrate, respectively, h_{wall} is the height of sidewalls, and L_{in} is the length of a side of a pattern enclosed by sidewalls in unit of μm. Since in this study the h_s and h_{wall} were fixed at 300 and 200 nm, respectively, the L_{in} is the only variable. From Eqs. (1) and (2), it is noted that the magnitude of compressive stress stored in the film generally increases with decreasing the pattern size and increasing the sidewall height, and it is influenced more by the pattern size.

Figure 4 shows the schematics of the cross-sectional film structures and the corresponding calculated compressive stresses. Here the compressive stresses induced only by sidewalls are shown. As shown in the Figure 4, the compressive stress, in general, is higher at the edges of the film than at the center. For bare Bi films with no patterns around, the magnitude of the compressive stress induced on the film is not large, and it disappears rapidly close to the edges of the film. A similar stress relief effect is observed for the 1000×1000 μm^2-sized patterns, as shown in Figure 4(b). However, the compressive stress level at the edges is higher than in the bare Bi case, indicating that the sidewall effect rapidly vanishes when using large patterns. This is why the two samples have almost identical Bi nanowire densities (see Fig. 2(b)). On the other hand, the stress enhancement effect by sidewalls appears over the entire pattern area for the 100×100 μm^2—sized patterns (type-A), as shown in Figure 4(c). More than two orders of magnitude of compressive stress are induced inside the film, as compared to either bare Bi films or large-patterned samples. This large stress reinforcement effect across the sample area results in the promotion of Bi nanowire growth aforementioned. We have not performed similar calculations on the same 100×100 μm^2—sized, but differently arrayed patterns (type-B) due to the increased complexity. Nonetheless, it is inferred that the stress induced by sidewalls is almost released through corners in contact with adjacent patterns, since even small channels are enough to relieve

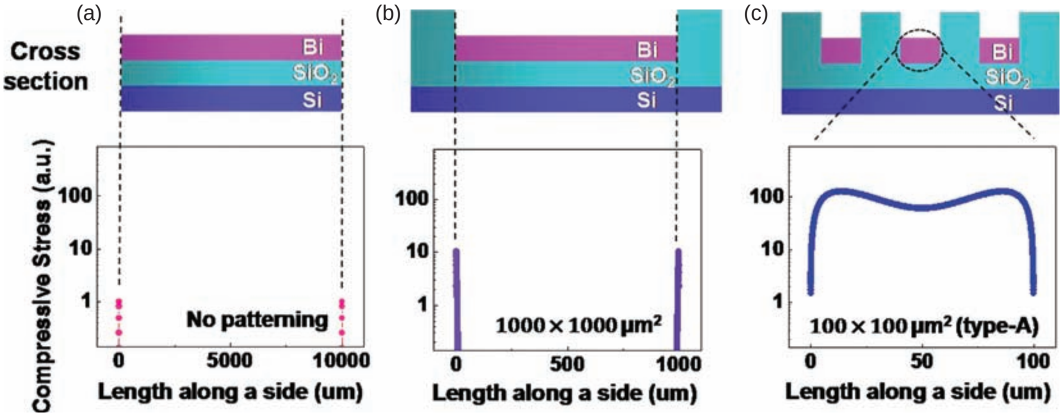

Fig. 4. Cross-sectional film structures and the corresponding compressive stress profiles in Bi films along a side: (a) bare Bi film, (b) Bi film in a 1000×1000 μm^2-sized pattern, (c) Bi film in a 100×100 μm^2-sized pattern.

stored stress. Therefore, it is important to control both pattern size and array to maximize the stress enhancement effect provided by the sidewalls.

4. CONCLUSIONS

In summary, we investigated the effects of compressive stress enhanced by sidewalls on the growth of Bi nanowires. It was found that the sidewall effect depends on the pattern size and array, and the density of Bi nanowires grown from Bi films in 100×100 μm^2—sized SiO_2 patterns is greater by a factor of seven compared to Bi nanowires grown on non-patterned bare Bi. By comparing the same 100×100 μm^2—sized patterns with and without sidewalls, the sidewall effect was further clarified. It was inferred that the compressive stress reinforcement by the sidewalls is the primary reason for the promoted Bi nanowire growth, and this inference was supported by size-dependent stress profile calculations. Our results indicate that the density of Bi nanowires can be increased by the enhanced compressive stress provided by the sidewall effect occurring in the optimized pattern size and array.

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