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Selective Growth of Silicon Nanowires on Glass Substrate with an Ultrathin a-Si:H Layer

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High density silicon nanowires (SiNWs) were selectively grown on a Cr/glass template with a very thin 5 nm thick a-Si:H layer at 500°C by a vapor–liquid–solid process using Au–Si nanoparticles as catalysts. SiNWs cannot be grown without the a-Si:H layer. Field emitters using these SiNWs were also fabricated. The threshold field of the fabricated field emitters was 15 V/μm. Furthermore, the field enhancement factor, β, of the fabricated SiNW field emitter was around 1700.
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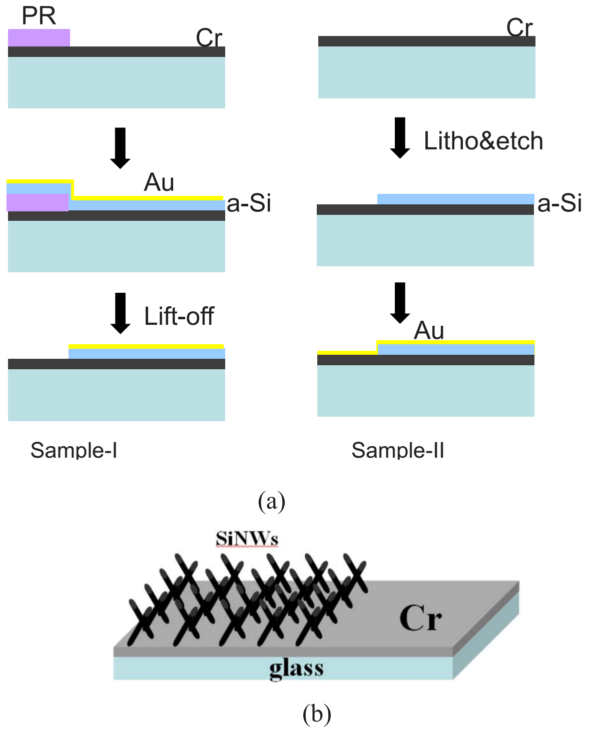
Field emitters are important devices that are potentially useful for flat panel displays. Over the past decades, field-emission properties of various materials have been extensively studied. Performances of field emitters depend strongly on the morphology and material density.[1-3] With a good geometric field enhancement factor, considerable attention has been focused on the use of one-dimensional (1D) nanotubes or nanowires as field emitters in recent years. For example, the field-emission properties of a carbon nanotube (CNT) have been extensively studied.[4-6] Field emitters based on other 1D materials, such as silicon, ZnO,[7,8] GeO,[9] SiO_2,[10] SnO_2,[11] SiCN,[12] MoO_3,[13] and CuO,[14] have also been demonstrated. Among these 1D materials, silicon is still the most promising candidate due to its well-established fabrication process in current integrated circuit industry. Silicon nanowires (SiNWs) can be grown by vapor–liquid–solid (VLS) growth,[15] solid–liquid–solid growth,[16] and oxide-assisted growth.[17] Nevertheless, most of these methods use bulk silicon wafer as the substrate to grow SiNWs.

Compared with Si substrates, glass substrates are transparent and low cost. Large area glass substrates are also commercially available. However, glass substrates are weak at high temperatures. Thus, it is difficult to prepare SiNWs on a glass substrate at high temperatures. Very recently, Shiu et al. used aqueous electroless etching to fabricate SiNWs from Si substrates. They then transferred the SiNWs onto alien substrates such as glass at low temperature. Using this method, they also demonstrated a SiNW-based hybrid solar cell on a glass substrate.[18]

However, the procedures used to transfer SiNWs onto a glass substrate are complex and might result in a low production yield. In this article, we deposited a thin a-Si layer on a glass substrate and then used the low temperature VLS process to grow the SiNWs.[19,20] Physical and field-emission properties of the fabricated SiNWs are also discussed.

Before the growth of SiNWs, a Corning 1737 glass substrate was wet-cleaned by acetone and deionized water followed by baking at 100°C for 10 min. A chromium (Cr) layer was subsequently deposited onto the chemically cleaned glass substrate by sputtering. The Cr layer served as the electrode during the field-emission measurement. Standard photolithography was then used to cover the electrode area by a photoresist. A 5 nm thick amorphous (a-Si) layer was also deposited onto the sample by plasma-enhanced chemical vapor deposition. Finally, a very thin layer of Au (i.e., ~5 nm) was deposited by sputtering to serve as the catalyst. The lift-off process was then used by immersing the sample in acetone with ultrasonic vibration to remove the photoresist and to expose the Cr electrode (i.e., sample I) for field-emission measurement. To clarify the role of the 5 nm thick a-Si:H layer, a sample with the a-Si:H buffer layer partially etched was also prepared (i.e., sample II). Detailed processing steps for these two samples are schematically shown in Fig. 1a.

The SiNWs were grown in a quartz tube furnace with an initial temperature of 550°C. After evacuating the furnace by a dry pump, the samples were inserted into the furnace and purged with N_2 gas. We then waited for 10 min at 550°C and then ramped down the temperature slowly to 500°C in 20 min. After stabilization, a mixture of 120 sccm SiH_4 and 400 sccm H_2 was introduced into the furnace to grow the SiNWs at 300 mTorr for 1 h. Figure 1b schematically depicts the SiNWs grown in sample I. After the growth, surface morphologies of the samples were characterized by a JEOL JSM-7000F field-emission-scanning electron microscope (FESEM), operated at 5–15 keV. A Renishaw micro-Raman system with a laser source of 633 nm was used to evaluate the optical properties of the as-grown SiNWs. Room-temperature field-emission properties of



(a)

(b)

Figure 1. (Color online) Schematic diagram of the sample (a) before and (b) after the growth of SiNWs.

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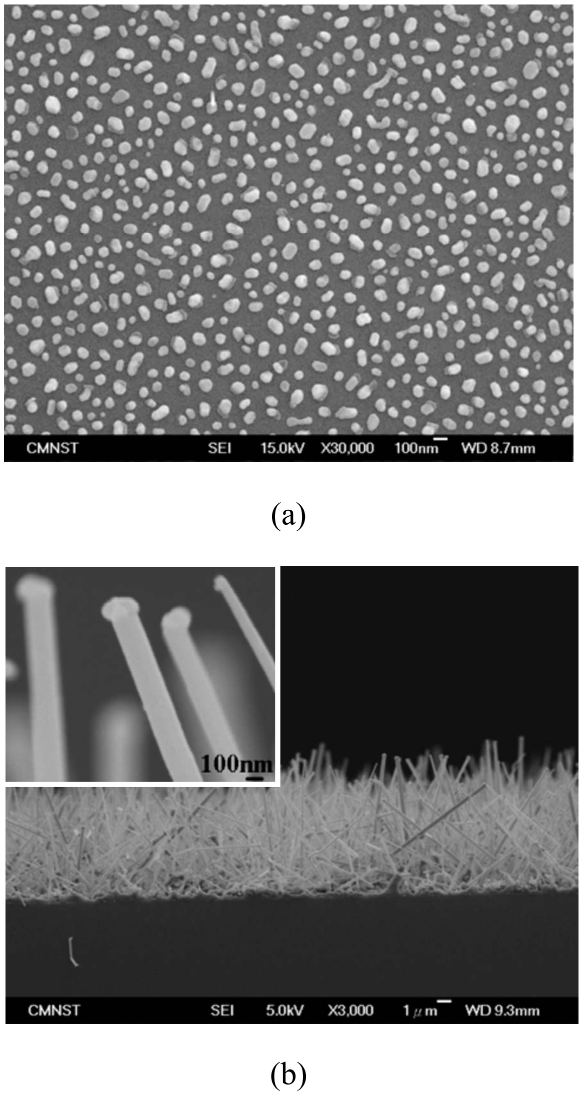

Figure 2. Scanning electron microscopy (SEM) images of (a) the unpatterned sample before the growth of SiNWs and (b) SiNWs grown by VLS process at 500°C The inset in (b) shows an enlarged SEM image of the SiNWs.

these SiNWs were also investigated. During the field-emission measurements, we placed the samples in a vacuum chamber with a pressure of 4×10^{-6} Torr. A tungsten probe with a diameter of 1.8 mm was then used as the anode, while the distance between the anode and the SiNWs was carefully controlled at 30 μm. A Keithley 237 high voltage source was then used to provide the sweeping electric field and to monitor the emission current.

Figure 2a shows the top-view FESEM image of sample I before the growth of SiNWs. After waiting for 10 min at 550°C, it can be seen that numerous nanoparticles[21] were formed on the sample surface. It can also be seen that these nanoparticles were distributed uniformly with an average size of 100 nm. The average size of the nanoparticles should depend on the thickness of the deposited Au and a-Si layers. Further studies are needed to clarify such relationships. Figure 2b shows the cross-sectional FESEM image of sample I after the growth of the nanowires. It can be seen that SiNWs with an average length of 7 μm were grown on the sample. The inset of Fig. 2b shows an enlarged FESEM image of the SiNWs. It can be seen from the enlarged image that the average diameter of the SiNWs was around 150 nm. One nanoparticle existed on the tip of each SiNW. This suggests that the growth mechanism of the nanowires was VLS. Figure 3 shows the titled FESEM image of sample II. It can clearly be seen again that high density SiNWs were grown on the region with the a-Si:H layer. In contrast, no SiNWs were found in the region where the a-Si:H layer was etched away. The clear boundary observed in Fig. 3 indicates that the SiNWs cannot be grown without the 5 nm thick a-Si:H layer. Previously, it has been demonstrated by Lee and Hwang that Au can be easily alloyed with Si.[22] It can be seen from the phase diagram that the eutectic temperature of Au–Si is 363°C. Thus, the Au–Si nanoparticle is formed after the 500°C thermal treatment. During the growth of SiNWs, these liquid metal nanoparticles also act as energetically favored sites to absorb the gas-phase reactants (i.e., SiH_4). By continuously introducing SiH_4 into the furnace, the Au–Si nanoparticles become supersaturated with silicon and the excess silicon freezes out at the interface of the Au–Si nanoparticles to form the 1D SiNWs [23] on the region with the a-Si:H layer. Instead of the Au–Si nanoparticles, pure Au nanoparticles were formed on the region without the a-Si:H layer. It is difficult for the liquid Au nanoparticles to absorb enough silicon from the introduced SiH_4 and to become supersaturated with silicon. As a result, no SiNWs were formed on the region without the a-Si layer.

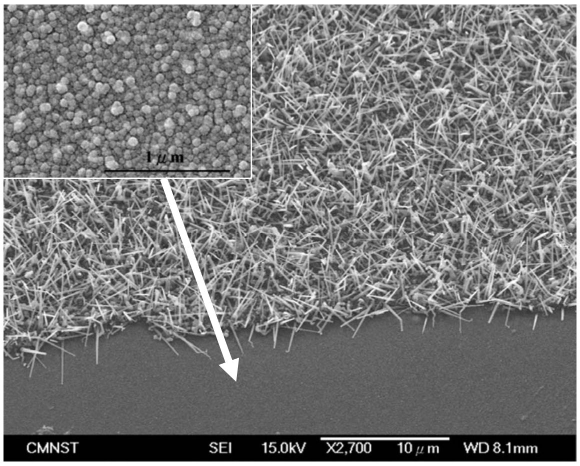

Figure 3. (a) Titled FESEM image of the patterned sample. (b) Phase diagram of Au–Si.

Figure 4 shows the Raman spectra measured from sample II. The solid line was measured from the area with the a-Si:H layer, while the dashed line was measured from the area without the a-Si:H layer.

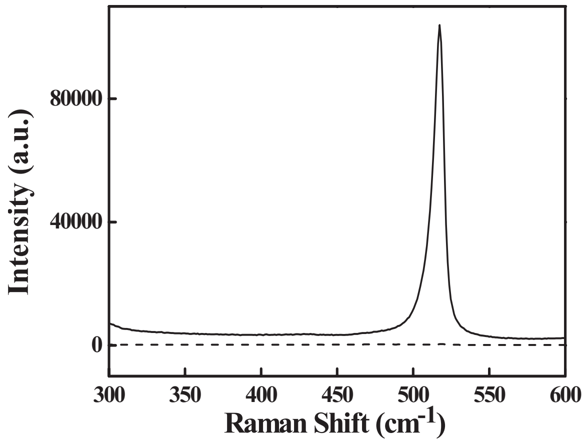

Figure 4. Raman spectra measured from the patterned sample. The solid line was measured from the area with the a-Si:H buffer layer, while the dashed line was measured from the area without the a-Si:H buffer layer.

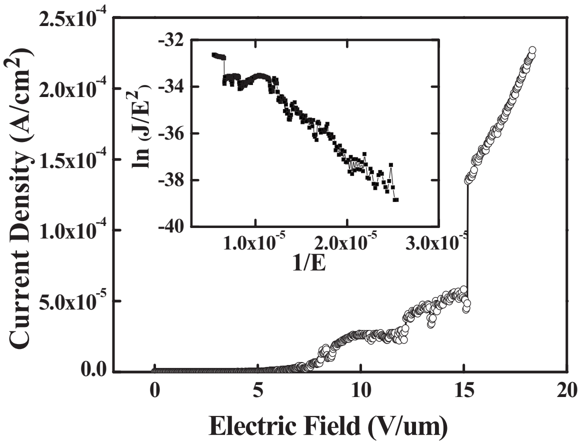

Figure 5. Emission current–voltage characteristics of the fabricated SiNWs. The inset is F-N plots of $\ln(I/V^2)$ against $(1/V)$.

Because SiNWs can be grown on the area with the a-Si:H layer, we observed a Si Raman peak at 520 cm^{-1}. The sharp peak suggests that the crystal quality of the SiNWs prepared in this study was reasonably good. In contrast, no obvious Si-related Raman signal could be observed from the area without an a-Si:H layer.

Figure 5 shows field-emission characteristics measured from sample I. As shown in Fig. 5, the field-emission current increased slowly when the applied bias was small. Also, the threshold voltage of this field emitter was 450 V (i.e., the applied electric field $E = 15\ \text{V}/\mu\text{m}$). At the threshold, the emission current was only around 0.13 mA/cm^2. As we further increased the applied bias, the emission current increased exponentially. Also the field-emission characteristics can be fitted by the Fowler–Nordheim (F-N) equation[24]

$$J = \frac{aE^2}{\beta^2\phi}\exp\left(\frac{-bd\phi^{3/2}}{\beta E}\right)$$

where J is the current density (A/cm^2), V is the applied voltage (V), β is the field enhancement factor, $\alpha = 1.56 \times 10^{-6}$ (A eV/V^2), $b = 6.83 \times 10^7$ $(\text{V/cm eV}^{3/2})$, and φ is the work function of the SiNWs, which is around 3.6 eV.[25] To further investigate the field-emission behavior of our SiNWs, we replotted $\ln(J/E^2)$ as a function of $1/V$, as shown in the inset of Fig. 5. From this F-N plot, the field enhancement factor, β, was around 1700. The β value depends on the geometry, the crystal structure, and the gap between the emitter and the anode. The β value observed from SiNWs prepared on the Si substrate ranges from 500 to 1800.[25-28] The β value observed from CNTs could reach 3392.[6] Compared with the β value observed from CNTs, the β value observed in this study is still much smaller. However, the 1700 β value observed from our SiNWs prepared on glass substrate suggests that the field-emission property of our SiNWs is comparable to those observed from the SiNWs prepared on the Si substrate.

In summary, high density SiNWs were selectively grown on a Cr/glass template with a very thin 5 nm thick a-Si:H buffer layer at 500°C by the VLS process using Au–Si alloy nanoparticles as catalysts. SiNWs cannot be grown without the 5 nm thick a-Si:H buffer layer. Field emitters using these SiNWs were also fabricated. The threshold field of the fabricated field emitters was 15 $\text{V}/\mu\text{m}$. Furthermore, the field enhancement factor, β, of the fabricated SiNW field emitter was around 1700.

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