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Silicon Nanowires by Aluminum-Induced Crystallization of Amorphous Silicon

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This paper discusses controlled studies on the effect of stress on the formation of silicon nanowires (SiNWs) produced by aluminum-induced crystallization (AIC) of plasma-enhanced chemical vapor deposited amorphous silicon (a-Si:H). The impact of stress on the growth of SiNWs was completely decoupled from other factors such as a-Si:H and Al deposition parameters and rapid thermal annealing conditions. This study shows, that AIC of a-Si:H can be used to fabricate SiNWs through the combination of rapid thermal annealing and stress adjustment.
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One-dimensional silicon nanostructures have attracted attentions in the last several years because of their great potential of being used within the fields of nanoscale electronics and photonics to build devices such as single-electron transistors, photodetectors, and bio/chemical sensors.[1-4] Currently, the techniques used to produce silicon nanowires can be grouped into two major categories, top-down and bottom-up fabrication methods. Top-down approaches employ lithography and etching to produce silicon nanostructures.[5,6] The lithography methods primarily include electron-beam and scanning probe lithography, and etching can be either dry plasma or wet chemical etching. Bottom-up fabrication techniques include chemical or physical vapor-phase deposition,[7] vapor-liquid-solid (VLS) crystal growth[8,9] mode, and solid-liquid-solid (SLS) growth mechanisms.[10,11] A typical vapor-phase deposition technique uses laser ablation of highly pure Si powder mixed with SiO_2 to fabricate SiNWs. The SiO_2 is used as a catalyst to enhance one-dimensional SiNWs growth. Within the process of using the VLS mechanism to grow SiNWs, metallic nanoparticles, Si-rich vapor, and high temperatures play important roles. During a VLS process, metal catalysts, usually Au, Ni, Ti, or Fe thin films, react with Si-rich vapor at high temperature and form supersaturated eutectic liquid droplets. As a result, the silicon elements in the gases precipitate onto a solid crystalline surface underneath the metal catalysts, and SiNWs grow with the droplets atop the wires. Growing SiNWs by using the SLS mechanism is similar to producing SiNWs by using the VLS mechanism, except for no Si-rich vapor is present during SiNWs growth. The growth of SiNWs through the SLS mechanism relies on interface diffusion between both silicon substrates/metal droplets and metal droplets/SiNWs at high temperatures. For example, a Ni thin film on a silicon substrate melts into eutectic liquid droplets at high temperatures in an Ar and H_2 environment. Si atoms in the substrate diffuse through the Si substrate/Ni droplets interface and precipitate atop the Ni droplets. As this process continues, SiNWs grow on the top of the metal droplets. It has been reported that H_2 and stress play critical roles in SLS mode growth.

Although many metals can be used as catalysts in the growth of SiNWs through either VLS or SLS mechanisms, to utilize SiNWs as building blocks for real nanoelectronic devices, it is desirable to select metals that are compatible with Si device fabrication. Al is a preferred metal because it has been widely employed in the semiconductor industry as a doping element or semiconductor-metal contacts. In addition, Al has been used to induce crystallization of plasma-enhanced chemical vapor deposited amorphous silicon (a-Si:H) for growing p-type heavily doped polycrystalline silicon films with large size grains for various applications such as thin-film transistors, sensors, solar cells, and display panels.[12-14] However, using Al to grow silicon nanowires through either traditional VLS and SLS mechanisms or aluminum-induced of crystallization of a-Si:H has not been reported. This paper reports, for the first time, successful fabrication of SiNWs using the combination of rapid thermal annealing of AIC of a-Si:H and adjusting stress in a-Si:H and Al films.

In this study, silicon wafers with thermally grown silicon oxide layers were selected as substrates. Amorphous silicon films of 100 nm thickness were deposited on the substrates using plasma-enhanced chemical vapor deposition (PECVD). The rf power, chamber pressure, substrate temperature, and SiH_4 flow rates were controlled at 20 W, 0.5 Torr, 250°C, and 85 sccm, respectively. After a-Si:H deposition, the samples were removed from the PECVD system and transferred to an evaporator for thermal deposition of 750 nm thick Al. It should be noted that exposing the samples to air created thin native silicon oxide layers between the a-Si:H and Al. When the aluminum depositions were finished, the wafers were divided into two groups, A and B, and Al films of 750 nm were deposited on the back surface of the samples from group B. Then, the samples from both groups A and B were annealed at about 800°C for 20 s in air. Finally, the remaining Al was removed by wet selective etching for the characterization of surface morphology and material properties. The characterization equipment included scanning electron microscopy (SEM), electron diffraction spectroscopy (EDS), and transmission electron microscopy (TEM).

Figure 1 shows SEM images collected from the samples (a) without a back surface Al coating and (b) with a back surface Al coating. The embedded image in Fig. 1b is an SEM image with higher magnification, illustrating details of the nanowires. Although both Fig. 1a and b reveal nanostructures, only Fig. 1b, the sample with back surface coating, exhibits nanowires. Since both samples have identical front surface thin-film structures and underwent the same heat-treatment, the appearance of different nanostructures must be the result of back surface coating.

Generally speaking, thin-film coating introduces stress and causes bending of substrates. To study the stresses induced by front surface films, the authors measured the curvatures of the wafers using a Tencor Flex2300 profilometer, and then estimated the stresses from the curvatures using Stoney's equation. The study showed that the depositions of a-Si:H on the front surfaces of silicon substrates resulted in a tensile stress in a-Si:H of about 450 MPa. The stress in a-Si:H introduced by thermally evaporated Al films was about 210 MPa. Therefore, the overall stress in a-Si:H and Al on the front surface of the samples in group A were about 650 MPa tensile and 210 MPa compressive, respectively. The stresses in a-Si:H and Al films on the front of samples from group B were different from those of samples in group A because back-surface Al coating changed the curvatures of the samples, and therefore the stresses in the a-Si:H and Al films on the front surfaces. The tensile

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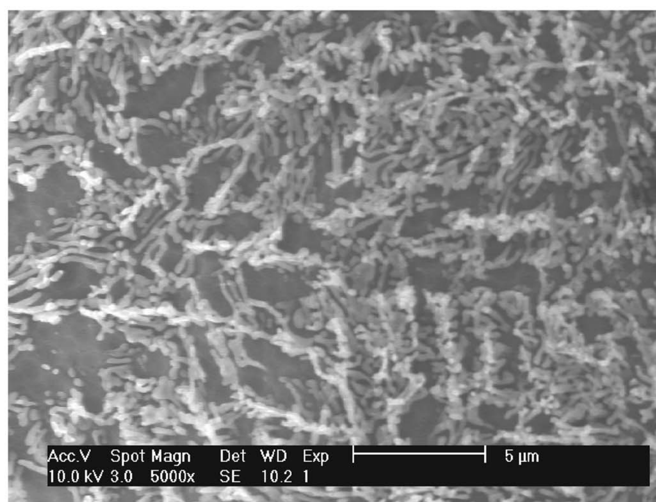
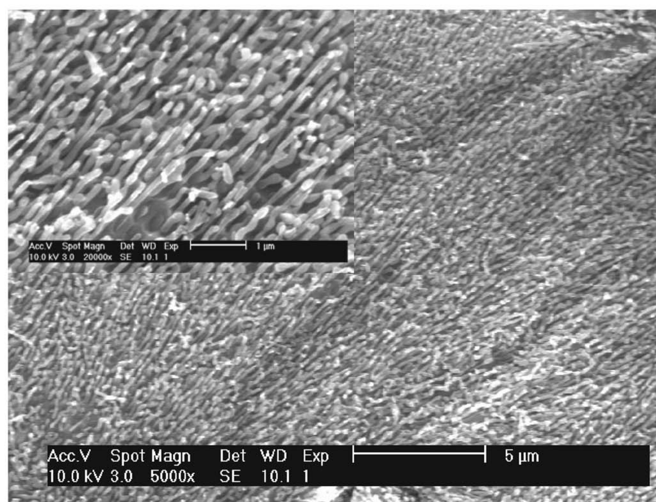


(a)



(b)

Figure 1. SEM images of nanostructures of the samples with and without back surface Al coatings. Figure 1a shows that the sample without the back surface coating does not have nanowires. Figure 1b illustrates that the sample coated with the back surface Al film has nanowire structures.

stress in a-Si:H was reduced by an Al coating on the back surface, while the compressive stress in the Al film on the front surfaces were enhanced by the back-surface Al coating.

The stress discussed above was obtained at room temperature. At the annealing temperature, the difference in the coefficients of thermal expansion of Si substrate, a-Si:H film, and Al film alters the stress in both a-Si:H and Al films on the front surfaces. The thermal expansion coefficient of Al is about $23 \times 10^{-6}/°C$, which is about nine time larger than that of a-Si:H ($2.5 \times 10^{-6}/°C$) and single crystalline silicon ($2.6 \times 10^{-6}/°C$).[15,16] Calculations show that the difference between the thermal expansions of a-Si:H and Al at 800°C introduces about 870 MPa of additional tensile stress in the a-Si:H and about 870 MPa compressive stress in the Al film on front surfaces. This means that, at 800°C, stresses in the a-Si:H and Al films of the samples from group A were about 1.52 GPa (tensile) and 1.09 GPa (compressive), respectively. Since Al films coated on the back surfaces of samples from group B were identical to the Al films on the front surfaces, the stress in a-Si:H induced by Al was approximately cancelled out, and the stress in the Al film on the front was further enhanced. The degree of the enhancement depends on the mechanical properties of the substrates, a-Si:H, and Al films and will be investigated in the future. The above analysis reveals that although the samples from groups A and B have identical front surface thin-film structures, the stresses in the a-Si:H and Al films are different. Therefore, it can be concluded that the stresses in the a-Si:H and Al films significantly affected the formation of the nanowires in this case. The finding that stress plays an important role in formation of nanowires is consistent with what has been reported in the literature.[17,18]

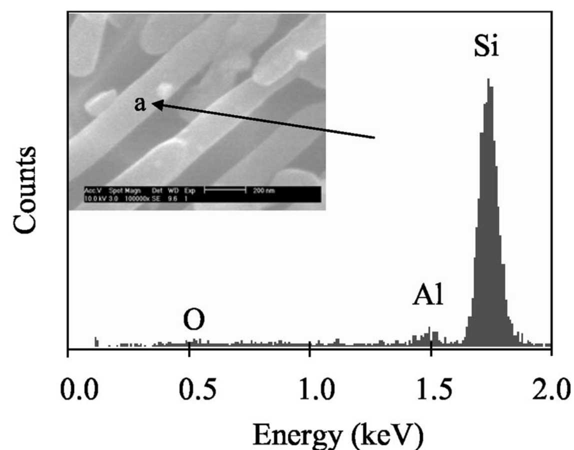


Figure 2. EDS spectrum taken from a nanowire shows a large amount of Si, some Al, and a small amount of O.

To verify that the nanowires fabricated are indeed SiNWs, the authors took EDS and electron diffraction from several nanowires. Figure 2 shows a representative EDS spectrum taken from a nanowire. The spectrum exhibits a large amount of Si, some Al, and a small amount of O. The O in the SiNW probably comes from native SiO_2 surrounding the SiNWs, similar to the finding previously reported in the literature,[17] and the Al may come from the Al underneath the SiNW. It is known that during AIC of a-Si:H, the interfusion between Si and Al results in layer exchange between the two films.[19] Figure 3 is an electron diffraction pattern collected from a nanowire that is detached from the substrate. The sample was prepared by scratching the nanowires from a substrate into an electron diffraction grid. The diffraction image shows both amorphous diffraction rings and crystalline diffraction spots, indicating that the

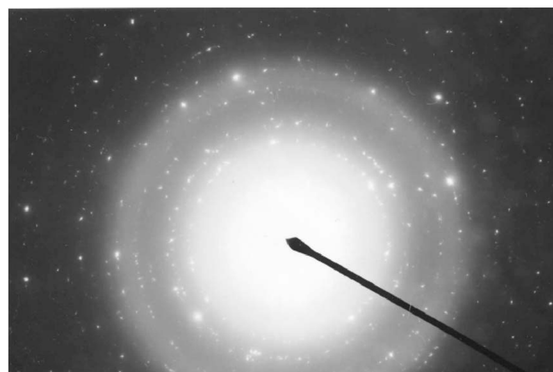


Figure 3. The electron diffraction image taken from a nanowire shows both amorphous diffraction rings and crystalline diffraction spots. This indicates that the nanowire probably consist of both amorphous and crystalline silicon.

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SiNW might be partially crystalline. The existance of amorphous silicon in the nanowires could be the result of the fast growth of the SiNWs during the rapid thermal annealing process.

The mechanism of growing SiNWs using AIC of a-Si:H is not clear and conceivably different from VSL or LSL. In cases of VLS and SLS growth, the Si source is provided by Si-rich vapor and bulk Si substrates, respectively. In addition, metal films used as catalysts in both cases are very thin. At high temperatures, these thin metal films melt into eutectic droplets to assist the growth of SiNWs. During the process of using AIC of a-Si:H to grow SiNWs, Al films were significantly thicker than the metals used in VSL and SLS growth and did not break into isolated nanodroplets during the high-temperature process. Studies on traditional AIC of a-Si:H show that crystalline silicon grains are created by Si diffusion from a-Si:H into Al film and grow inside the Al films. Therefore, a possible mechanism of growing SiNWs using AIC of a-Si:H is that during rapid thermal annealing, Si atoms in a-Si:H (*i*) diffused into Al through the eutectic layer between a-Si:H and Al (the eutectic point of Si-Al being 577°C), (*ii*) nucleated and crystallized at defects that randomly distributed in the Al films, and (*iii*) self-rearranged in the Al films along preferred directions due to Gibbs free energy change in the system. The exact mechanism will be investigated in the future.

In summary, this study investigated the effect of stress on formation of SiNWs by completely decoupling the stress from structural and process parameters. The results of this controlled study shows that the stresses in a-Si:H and Al play important roles in forming SiNWs, although it is not clear which stress is more important. This paper reports the fabrication of SiNWs through the combination of rapid thermal annealing and altering stress in a-Si:H and Al thin films.

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