Catalytic Growth of Si Thin Film using Very High Frequency Plasma Enhanced Chemical Vapor Deposition

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Abstract

The catalytic growth process of silicon (Si) thin film was done as our preliminary experiment on our research in order to develop silicon nanowire (SiNW) materials. The aurum (Au) and nickel (Ni) catalyst in the form of very thin film have been grown on wafer silicon substrate using thermal evaporation method. Both Au and Ni catalysts films formed by this method have been annealed at temperature of 450°C and 600°C, respectively. The Si thin films were deposited for 30 minutes by Plasma Enhanced Chemical Vapor Deposition (PECVD) using plasma frequency of 70 MHz at chamber pressure of 400 mT, and growth temperature of 350°C. The Silane (SiH₄) gas as Si source was flowed pass through the chamber at flow rate of 70 sccm. The optical reflectance of the Si thin film was measured by reflectance spectroscopy in the range of wave length 400-2400 nm. Based on the reflectance patterns, smoothness and thickness of the film can then be determined. The energy band gap E_{σ} was indicated from the end position of the oscillation peak. It was 1.834 eV and 2.129 eV for the films grown on the Au and Ni catalyzed substrate, respectively. The surface morphology of the films by scanning electron microscope (SEM) showed that Au and Ni catalyst gave initial result towards Si columns formation.

1. Introduction

Semiconductor Nanowires (NWs), one of one-dimensional structure, is explicitly mentioned as realistic addition in a special section on Emerging Research Devices in the *International Technology Roadmap for Semiconductors* [1]. Applications of the NWs through of bottom-up paradigm is possible because the rationality for controlling of key nanomaterial parameters such as chemical composition, structure, size morphology, and doping, that determine electronic and optoelectronic properties specially to predictable device function [2]. Both the scientific and technical communities take an interest in NWs because of the possibilities for greatly reduced device dimensions, radial epitaxial capping, and axial growth of lattice mismatched structures [3].

A semiconductor NWs, including silicon nanowire (SiNW), is a solid rod with a diameter less then 200 nm composed one or several semiconductor materials. SiNW can be synthesized using many techniques, such as molecular or chemical beam epitaxy, vapor phase epitaxy (chemical vapor deposition), and laser ablation. The nanowires have been growth through both vapor-liquid-solid (VLS) and vaporsolid-solid (VSS) mechanisms [3-5]. The particular type of nanowire is typically grown at a metal particle (as a catalyst) on a substrate surface. The metal particle size determines the wire diameter. Furthermore, it is the process known as catalytic growth process.

Plasma enhanced chemical vapor deposition (PECVD) method used to growth carbon nanotube (CNT) material through catalytic growth process [6-7]. Hence, we are concerning our research to developing SiNW material using technique based on PECVD. First step of the work is growing silicon thin film at catalyzed wafer silicon substrate. The catalytic growth process of Si thin film was done as our preliminary experiment on our research. Both optical properties and surface morphology of the film was characterized in order to determine next step to develop SiNW material, specially, to controlling growth parameters of catalyst and SiNW materials. This paper reported our results of the preliminary experiment.

2. Experiment

The wafer Si (100) substrates were sequentially cleaned by acetone and methanol for 5 minutes, each followed by washing in the pure water for 5 minutes. They were dipped into 20 % HF solution for 3 minutes to remove native SiO₂ on the Si substrates, then they were washed again using pure water. Finally, the substrates were blown using dry nitrogen.

Immediately, the substrate introduced into thermal evaporator and coated with Au or Ni layer. The catalyst material (Au or Ni) was grown using thermal evaporation method for 15 second. By this way, we wish to get very thin film of catalyst material. Nanosized Au or Ni particles are formed on the substrate by annealing very thin Au or Ni film at temperature of $450 \,^{\circ}$ C or $600 \,^{\circ}$ C, respectively. Both Au and Ni catalyzed substrate were then placed in the reaction chamber of the PECVD system. The vacuum in the chamber is achieved and maintained at a level of 400 mT by an oil rotary pump ULVAC EC810.

The specimen temperature was held on 350 ^oC by temperature controller. The silane gas as Si source was flowed pass through the chamber at flow rate of 70 sccm. Mass flow controller was used to control the level of the supplied gas. The Si thin films were deposited for 30 minutes by PECVD using plasma frequency of 70 MHz. It is known as very high frequency (VHF) PECVD technique. The plasma generated by rf generator at power of 25 watt. Fig. 1 shows the plasma in the reaction chamber during the growth process.

The optical properties of the films were measured by optical reflectance spectroscopy in the range of wavelength of 400-2400 nm with resolution of 2 nm by Shimadzu UV-

3101PC UV-VIS-NIR Scanning Spectrophotometer. Based on the reflectance patterns, smoothness and thickness of the film can than determined. In addition, the energy band gap E_g was indicated from the end position of the oscillation peak [8-10]. The surface morphology of the thin film was characterized using JEOL JSM6360LA Analytical Scanning Electron Microscope.



Figure 1: Plasma in the reaction chamber of PECVD system, during the growth process.



3. Results and Discussion

Figur 2: The optical reflectance spectra of Si thin film grown using VHF-PECVD technique on (a) Au, and (b) Ni catalyzed substrate.

The results of the room temperature reflectance spectra of the Si thin film samples are shown on Fig. 2 and 4. Fig. 2 shows reflectance against wavelength of incident photon for the sample catalyzed by Au and Ni, and Fig. 4 shows reflectance versus photon energy.

Orderliness of oscillation patterns of optical reflectance indicated perfection of the excitonic and band to band resonances of the material. These resonances perfection depend on the homogeneous surface of the film which caused the incident beam to the film scattered to appropriate direction. Hence, smoothness of the film can be predicted from the orderliness of oscillation patterns. The Si thin film grown on Au catalyzed substrate (Fig 2a) has the oscillation pattern of optical reflectance less in order than the other one (Fig 2b). Agree with the above description, this indicated that the excitonic and band to band resonance of the material were less perfect due to less homogeneous surface of the film. In the other word, the surface of Si thin film grown on Ni catalyzed substrate smoother than the surface of the Si thin film grown on Au catalyzed substrate.

The thickness d of each sample was calculated from these oscillation patterns of optical reflectance through te well know interference equation [9]:

$$d = \frac{1}{2} \left(\frac{\lambda_1 \lambda_2}{n_1 \lambda_2 - n_2 \lambda_1} \right) (N - 1)$$

where *N* is the number of maxima from λ_1 to λ_2 , n_i is the refractive index at the maximum λ_i . The number of the peak of the reflectance oscillation related to the thickness of the film. The thickness values of the thin film Si grown on Au catalyzed substrate and grown on Ni catalyzed substrate are calculated from 6 and 8 oscillation peaks were 77,05 nm and 86,68 nm, respectively. The results were similar to the thickness value of the films analyzed by SEM analysis (Fig. 3).



Figure 3: Morphological surface and cross sectional SEM images (tilt of 10⁰) of Si thin films grown using VHF-PECVD technique on (a) Au, and (b) Ni catalyzed substrate.

Although the same deposition conditions were used for both Au and Ni catalyzed substrate, the film growth process is different in those two materials. Fig. 3 shows the morphological surface and cross sectional SEM image (tilt of 10^{0}) for two samples, one deposited on Au catalyzed substrate (Fig. 3a) and another one deposited on Ni catalyzed substrate (Fig. 3b). The Si thin film of samples on Fig. 3b has smoother and larger grain size compared to sample on Fig. 3a. In addition, there are differences in the film thickness, agree with the results of the optical reflectance. The surface morphology of the films showed that Au and Ni catalyst gave initial result towards Si columns formation.



(b)

Figure 4: The optical reflectance spectra of Si thin film grown using VHF-PECVD technique on (a) Au, and (b) Ni catalyzed substrate. The last position of the oscillation peak corresponding to the value of energy band-gap

Fig. 4 shows the room temperature optical reflectance spectra of Si thin film deposited on Au and Ni catalyzed substrate. The last position of the oscillation peak related to the band-to-band transition of the films corresponding to the value of energy band-gap (E_g). It was 1.834 eV and 2.129 eV for the films grown on the Au and Ni catalyzed substrate, respectively. These band-gap energies are larger compared to the nature of the band-gap in Si nanowire has been investigated by means of *ab initio* calculations [11].

4. Conclusions

The Si thin film can be deposited through catalytic growth process. In order to get more thickness films required longer time of deposition. The surface morphology of the films showed that Au and Ni catalyst gave initial result towards Si columns formation. The band-gap energies are larger compared to the nature of the band-gap in Si nanowire has been investigated by means of *ab initio* calculations.

5. Acknowledgements

The research was supported by Lembaga Penelitian dan Pengabdian pada Masyarakat of Bandung Institute of Technology through Program Riset KK ITB 2007.

6. References

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