P-μc-$Si_{1-x}Ge_x$:H thin film by VHF-PECVD*

SHANG Ze-ren, ZHANG Jian-jun, ZHANG Li-ping, HU Zeng-xin, XUE Jun-ming, ZHAO Ying, and GENG Xin-hua**

Key Laboratory of Photo-Electronics Thin Film Devices and Technique of Tianjin, Key Laboratory of OPtoelectronic Information Science and Technology of Education Ministry, Institute of Photo-Electronics Thin Film Devices and Technology, Nankai University, Tianjin 300071, China

(Received 29 September 2007)

In this paper, a series of boron doped microcrystalline hydrogenated silicon-germanium (p-μc-$Si_{1-x}Ge_x$:H) was deposited by very high frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) from SiH_4 and GeF_4 mixtures. The effect of GeF_4 concentration on films' composition, structure and electrical properties was studied. The results show that with the increase of GeF_4 concentration, the Ge fraction x increases. The dark conductivity and crystalline volume fraction increase first, and then decrease. When the GC is 4%, p-μc-$Si_{1-x}Ge_x$:H material with high conductivity, low activation energy (σ= 1.68 S/cm, E_g = 0.047 eV), high crystalline volume fraction (60%) and with an average transmission coefficient over the long wave region reaching 0.9 at the thickness of 72 nm was achieved. The experimental results were discussed in detail.

CLC numbers: TN304.2$^+$3 **Document code:** A **Article ID:** 1673-1905(2008)02-0130-3

DOI 10.1007/s11801-008-7137-0

Microcrystalline hydrogenated silicon-germanium (μc-$Si_{1-x}Ge_x$:H) is a promising low-band-gap material for bottom cell in multi-band gap solar cells[1], due to higher absorption coefficient for visible light and insensitivity against light-induced metastable changes[2, 3] . Moreover, its band gap can be tailored by changing the Ge content to match longer wavelengths of solar spectrum. However, so far, the p-layer used for the μc-$Si_{1-x}Ge_x$ thin film solar cells with the p-i-n structure was usually p-type microcrystalline silicon, which results in lattice mismatch and band gap offset between p- and i-layer. As a result, a p-μc-$Si_{1-x}Ge_x$:H layer with proper Ge content and higher conductivity is needed for improving the interface between p- and i-layer of the cell, and sufficient crystalline volume fraction is needed to promote the nucleation of the intrinsic layer at the p/i interface.

This paper reports the effects of GeF_4 concentration on the characteristics of p-μc-$Si_{1-x}Ge_x$:H thin films. The results showed that with the increase of GC, the Ge fraction x increases slowly first and then increases linearly, the dark conductivity increases first and then decreases, and the crystalline volume fraction of p-type microcrystalline silicon germanium films decreases.

All p-μc-$Si_{1-x}Ge_x$:H thin films were prepared by VHF-PECVD using a $SiH_4/GeF_4/B_2H_6/H_2$ gas mixture on glass at 70 MHz, 60 Pa, 180 °C and the background system vacuum was lower than 3.5×10^{-5} Pa. The distance between two electrodes was 1.6 cm. We define a GeF_4 concentration as the source gas flow rate ratio, $[GeF_4]/[GeF_4]+[SiH_4]$, where $[GeF_4]$ was varied from 0 to 2.5 sccm at a fixed $[SiH_4]$ of 5sccm. The other deposition parameters, such as the discharge power deposition time and the thickness of the films, were 10 W, 15 minutes and about 72 nm, respectively. Besides, the silane concentration ($[SiH_4]/[SiH_4]+[H_2]$) was about 1% and the doped ratio ($[B_2H_6]/[SiH_4]+[GeF_4]$) was 0.5%. The Ge fraction x was measured by XRF and the dark current of material was measured by Keithley 520 at room temperature using Al coplanar contact electrode, and then the dark conductivity was calculated. The crystalline volume fraction (X_c) was evaluated by Raman scattering measurements and $X_c = (I_{500} + I_{520})/(I_{480} + I_{500} + I_{520})$ [4], the ratio of the integrated intensities of the Gaussian peaks fitted to Raman signal, attributing to crystalline grains (at 500 and 520 cm^{-1}) and disordered regions (at 480 cm^{-1}), was regarded as a semi-quantitative value for crystallinity volume fraction.

Fig.1 shows the Ge fraction x in the series of p-μc-$Si_{1-x}Ge_x$:H films as a function of GeF_4 concentration in the gas-phase. x represents the atomic ratio of germanium in the films, which was estimated by XRF. With the GeF_4 concentration increasing, x shows a slow increase at smaller GeF_4 concentrations, followed by a linearly increase at larger GeF_4

---

* This work has been supported by National Basic Research Program of China ("973" Project, No.2006CB202602, 2006CB202603), the National Natural Science Foundation of China (No. 60437030), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars of the State Education Ministry.

** E-mail: zrshang@mail.nankai.edu.cn

concentrations.

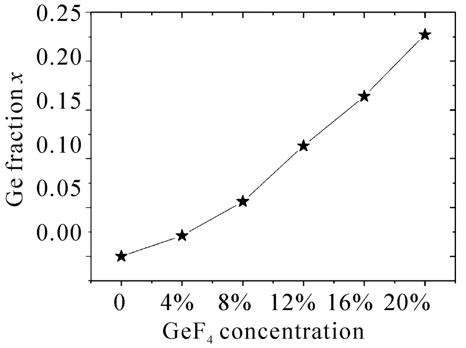

Fig.1 Ge fraction x in the p-μc-Si$_{1-x}$Ge$_x$:H films as a function of GeF$_4$ concentration in the gas-phase.

T. Matsui[5] reported a different change in μc-Si$_{1-x}$Ge$_x$:H prepared from SiH$_4$-GeH$_4$ gas mixture, in which the Ge fraction x increased steeply first and then increased slowly. The main reason for this is that the Ge-F bond is more steady than Ge-H bond, therefore the GeF$_4$ has a higher decomposition energy than GeH$_4$ and thus the growth rate of Ge precursors is lower than Si precursors. The difference between them can be attributed to this. Besides, the incorporation of boron was perhaps another reason for the different change.

Fig.2 shows the Raman spectra of the p-μc-Si$_{1-x}$Ge$_x$:H films. The peak positions of Si-Si, Si-Ge and Ge-Ge transverse optic (TO) vibrations at ~510, ~400 and ~280 cm^{-1}, respectively, confirm the crystalline matrix of SiGe alloy. The peak position of Si-Si vibration is sensitive to Ge content. By increasing GeF$_4$ concentration, Si-Ge peaks appear, followed by the appearance of Ge-Ge peaks while maintaining the crystalline structure.

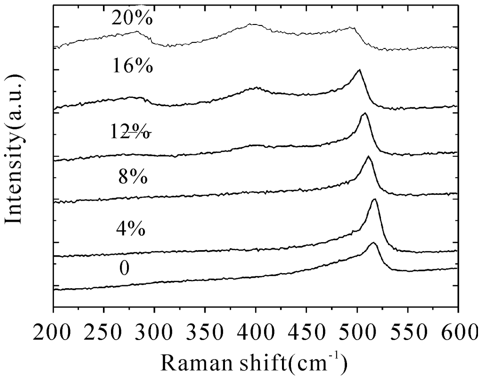

Fig.2 Raman spectra of p-μc-Si$_{1-x}$Ge$_x$:H films deposited under different GeF$_4$ concentrations.

The Si-Si and Ge-Ge peaks shift to lower and higher wave numbers, respectively, by alloying, because the Si-Si and Ge-Ge bonds receive tensile and compressive stress due to the difference between the bond lengths of Si and Ge. We also calculated the crystalline volume fraction of the films by formula $(I_{500} + I_{520})/(I_{480} + I_{500} + I_{520})$ and found that the film deposited under 4% GeF$_4$ concentration had the highest crystalline volume fraction of 60% and that the crystalline volume fraction decreased with the GeF$_4$ concentration increasing. This is accordant with the results of the dark conductivity ever reported. Besides, it indicates that the introduction of GeF$_4$ promotes the nuclei-formation capability at the initial stage of film growth and then results in the crystalline growth[6].

In Fig.3, the results on dark conductivity measurements are plotted versus GeF$_4$ concentration. It is obviously that the dark conductivity increased when little germanium was incorporated into the microcrystalline silicon film. However, the dark conductivity decreased by 7 orders of magnitude when increasing GeF$_4$ concentration from 12% to 20%.

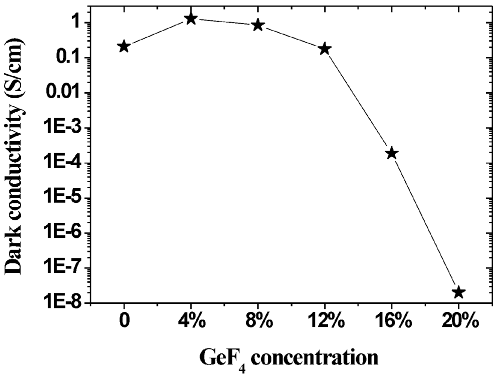

Fig.3 Dark conductivity as a function of GeF$_4$ concentration.

From Hall-effect measurement, we confirmed that the steeply decreased dark conductrvity arises from an appreciable free-hole annihilation at GC>12%. When GeF$_4$ concentration is over a certain value, the defect density increases faster with the GeF$_4$ concentration increasing, thus induces the free-hole annihilation and deteriorates the carrier transport. On the other hand, as we know, the conductivity increases with the increase of the crystalline volume fraction of the microcrystalline silicon film[7].

As we know, the transmission of the p-layer plays an important role on the performance of PIN type microcrystalline hydrogenated silicon-germanium solar cells.

A higher transmission can let more light pass through the p-layer and more photons can be absorbed by the i-layer. Therefore, the transmission property was measured for the film which had the highest dark conductivity. The result was shown in Fig.4.

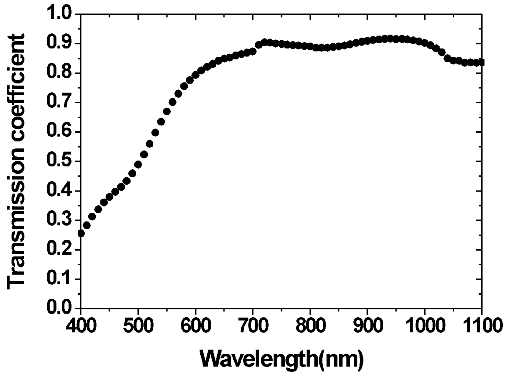

Fig.4 Transmission of the p-μc-$Si_{1-x}Ge_x$:H film

μc-SiGe solar cell is usually used as the bottom cell in multi-junction structure solar cells. So most photons of the visible light range are absorbed by the top and middle cell. Thus the analysis of spectral transmittance in the wavelength range larger than 700 nm is very important for the bottom cell. In Fig.4, we can see that the film has an average transmission coefficient of 0.902 over the wavelength range from 700 nm to 1100 nm, which means that the spectral transmittance of p-layer deposited with a GeF_4 concentration of 4% is suitable for the windows layer of μc-SiGe solar cell.

A series of boron doped microcrystalline hydrogenated silicon-germanium were deposited by VHF-PECVD at different GeF_4 concentrations. The results showed that, with the increase of GC, the Ge fraction x increases, and the dark conductivity increases first and then decreases. When the GC is 4%, a p-μc-$Si_{1-x}Ge_x$:H material with high conductivity, low activation energy (σ = 1.68 S/cm, Eg = 0.047 eV), high crystalline volume fraction (60%) and with an average transmission coefficient over the long wave region reaching 0.9 at the thickness of 72 nm was achieved.

References

[1] G.Ganguly, T.Lkeda, T.Nishimiya, K.Saitoh, M.Kondo, and A.Matuda Appl.Phys.Lett., **69** (2002), 519.

[2] Jatindra K.Rath, F.D.Tichelaar, and Ruud E.I.Schropp, Solar Energy Material & Solar Cells, **74** (2002), 553.

[3] M.Isomura, K.Nakahata, M.Shima, S.Taira, K.Wakisaka, M. Tanaka, and S.Kiyama, Solar Energy Material & Solar Cells, **74** (2002), 519.

[4] A.K.Barua, Arindam Sarker Swati Ray, Technical Digest of the international, PVSEC-12

[5] T.Matsui, K.Ogata, M.Isomura, and M.Kondo, J.Non-cryst. Solids, **352** (2006), 1255.

[6] Jianjun Zhang, Kousaku Shimizu, Ying Zhao, Xinhua Geng, and Jun-ichi Hanna, phys,stat.sol.(a), **1-16,** (2006).

[7] Feng Zhu, Changchun Wei, Ying Zhao, Xiaodan Zhang, Yantao Gao, and Xinhua Geng, PVSEC-20