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Determination of Optical Band Gap and Germanium Content of Hydrogenated Micro-Crystalline $Si_{1-x}Ge_x$ Films by Ultraviolet-Visible and Auger Electron Spectroscopy Measurements

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We report a reasonable method for determination of optical band gap (E_g) and germanium content (x) of hydrogenated micro-crystalline silicon-germanium (μc-$Si_{1-x}Ge_x$:H) thin-film by using ultraviolet-visible (UV-visible) and Auger electron spectroscopy (AES) measurements. For reasonable extraction of the E_g of μc-$Si_{1-x}Ge_x$:H film, we used a plot of $(\alpha h\nu)^{1/4}$ versus photon energy (E_{ph}) for a wide range of E_{ph}. The simplest explanation of the 1/4 power could be a superposition of absorptions from micro-crystalline structure. We also measured the x as a function of E_g of the μc-$Si_{1-x}Ge_x$:H thin-film. Using UV-visible, E_g was measured to be varying from 1.043 to 1.079 eV and x was extracted to be between 0.107 to 0.188. From AES measurements, the E_g was extracted between 1.045 to 1.075 eV while x was measured between 0.110 to 0.182. The results of the comparative analysis of UV-visible and AES measurement were performed.

Keywords: Optical Band Gap, Ultraviolet-Visible, Germanium Content, Auger Electron Spectroscopy, Hydrogenated Micro-Crystalline Silicon-Germanium.

1. INTRODUCTION

In the recent years, hydrogenated silicon-based materials are one of the attractive materials for thin-film electronics including thin film photovoltaic devices[1–3] and thin-film transistors (TFTs).[4,5] Among these applications, amorphous silicon have been used in solar cells and TFTs have the prospect of commercialization. However, the amorphous active layer in these electronics suffer from instability due to the light induced degradation and low carrier mobility.

Micro-crystalline silicon-based materials, especially hydrogenated micro-crystalline silicon-germanium (μc-$Si_{1-x}Ge_x$:H), has some advantages in enhancing the optical absorption of solar spectrum for bottom solar cell of multi junction thin film solar cells by adjusting the Ge content in the material. In the TFT, its carrier mobility can also be enhanced by adjusting the Ge content.

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The estimation of optical band gap (E_g) by using the optical absorption coefficient (α) as a function of photon energy (E_{ph}), is a widely used method. The Tauc equation, that is used in most of these measurements, relating the α to the E_{ph} is:[6,7]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_{opt}) \tag{1}$$

where E_{opt}, $h\nu$ and A are the optical energy gap, photon energy and a constant, respectively, where $n = 2$. The properties of hydrogenated micro-crystalline silicon materials are not well understood because of the complexity of its structure, therefore the $n = 2$ does not always give satisfactory results, and the Tauc plot is not always a straight line, as indicated by the Eq. (1).

In order to find a solution to this situation, several attempts have been made in the past, few of them are based on finding a suitable value of n in Eq. (1) so that the modified Tauc's plot looks as expected. Recently, Yan et al. estimated the band gap of nc-Si:H using a plot of $(\alpha h\nu)^{1/5}$ versus E_{ph} (or $n = 5$) to show a better linearity than Tauc plot using $n = 2$,[3] where E_{ph} is $h\nu$ the photon energy. However, this $n = 5$ may not be applicable for various other types of amorphous- or micro-crystalline silicon-germanium films. Therefore, we performed a detailed study of the μc-$Si_{1-x}Ge_x$:H to measure optical gap of these films with an empirically modified version of Eq. (1).

In this work, we estimated the E_{opt} of the μc-$Si_{1-x}Ge_x$:H films by using a plot of $(\alpha h\nu)^{1/4}$ versus E_{ph} (or $n = 4$). Using Auger electron spectroscopy (AES) measurement, the germanium content (x) was estimated. Finally, we propose an empirical method of estimating germanium content within the film from the UV-vis measurement.

2. EXPERIMENTAL DETAILS

The In the experimental studies, 300 nm thick μc-$Si_{1-x}Ge_x$:H films were deposited on glass substrates (Corning, Eagle 2000) and crystalline silicon wafers by using plasma enhanced chemical vapour deposition. These films were used for optical characterization with the help of ultraviolet-visible (UV-vis) spectroscopy and structural characterization by using AES. Before the deposition, the glass and crystalline silicon wafer substrates were cleaned in the following method. It was immersed in acetone and methanol for ultrasonic washing and removal of impurities on their surfaces. And then the glasses were washed with deionized (DI) water, and finally dried in a high purity N_2 gas stream. The films that were deposited on crystalline silicon wafers were used later to analyze its chemical composition. The wafer substrates were also cleaned before the film deposition, by immersing in buffered hydrofluoric acid for 30 seconds to remove native oxides from the wafer surfaces, washing with DI water again, and using N_2 gas stream to remove the remaining moisture. The deposition conditions of μc-$Si_{1-x}Ge_x$:H films were as follows; the power density, deposition temperature and base/working pressure were 32 W/cm^2, 200 °C and 6.7×10^{-5}/130 Pa, respectively. For deposition of μc-$Si_{1-x}Ge_x$:H films, silane (SiH_4), germane (GeH_4) and hydrogen (H_2) were used. The SiH_4 gas flow rate was fixed at 5 sccm for all samples and the GeH_4 gas flow rate was varied from 1 sccm to 3 sccm. The H_2/SiH_4 gas flow ratio was changed from 40 to 100. The thickness of μc-$Si_{1-x}Ge_x$:H films were estimated by spectroscopic ellipsometry. The E_{opt} of the μc-$Si_{1-x}Ge_x$:H films were estimated by using optical transmittance and reflectance measured from the UV-vis. In order to analyze the film compositions, AES was also employed. Crystallinity of the films were estimated by using Raman spectroscopy.

3. RESULTS AND DISCUSSION

Figure 1 shows the variation in crystalline volume fraction (X_c) of μc-$Si_{1-x}Ge_x$:H thin films due to the variation in

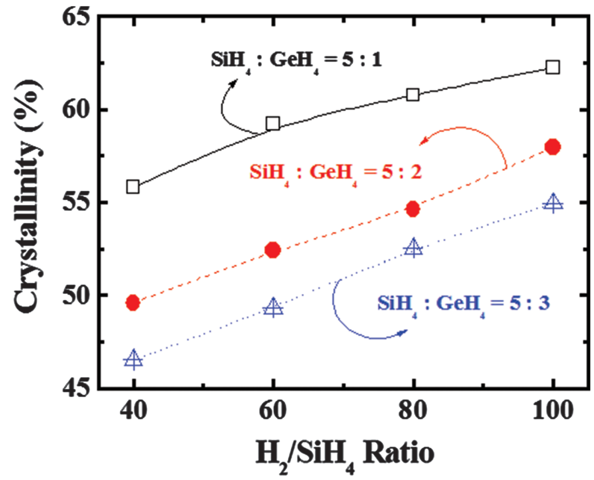

Figure 1. The crystallite volume fraction of μc-$Si_{1-x}Ge_x$:H thin films, measured by Raman spectroscopy, for films prepared with different SiH_4, GeH_4, H_2 gas flow ratios.

GeH_4 and H_2 flow rates. The plots show a nearly linear increase in micro-crystallinity for increased hydrogen dilution during film growth, which follows the conventionally known method of preparing films with increased micro-crystallinity at a higher hydrogen dilution. However, it is to be noted that micro-crystallinity decreases with increased germane flow rate. When the SiH_4/GeH_4 gas ratio was fixed at 5/1, the X_c was observed to increase from 55.82% to 62.27% due to the increase of H_2/SiH_4 gas ratio from 40 to 100. This observation is similar to that reported by Ito et al.[8] and Tang et al.[9] Similar measurements were performed using SiH_4/GeH_4 as 5/2, and 5/3, As shown in the Figure 1.

Looking into the three traces it can be pointed out that, when the SiH_4/GeH_4 gas ratio was changed from 5/1 to 5/3 at a constant H_2/SiH_4 gas flow ratio as 100, the X_c decreased from 62.27% to 54.95%. In this study, X_c was over 50% for all of H_2/SiH_4 ratios when SiH_4/GeH_4 was 5/1, however it could be below 50% for low H_2/SiH_4 ratio when SiH_4/GeH_4 gas ratio was 5/2 and 5/3. That means that higher GeH_4 flow rates hinders formation of micro-crystallinity within the films.

Figure 2 shows the changes in E_{opt} of the micro-crystalline films. The optical gap was measured using $n = 4$ in Eq. (1). Here the three traces are for three different germane flow rates, whereas the trend of the traces depend upon the hydrogen dilution. The traces show that the optical gap of the films decrease nearly linearly with increased hydrogen dilution. For any fixed H_2/SiH_4 ratio, the E_{opt} decreased as GeH_4 flow rate increased, this follows the conventional method of lowering band gap of amorphous silicon alloy by using higher germane flow rate. Comparing the Figures 1 and 2, it is clear that the E_{opt} of μc-$Si_{1-x}Ge_x$:H thin films increased with decreased crystallinity and increased Ge content, a trend similar to that reported by Pethuraja et al.[10] In reality, when the

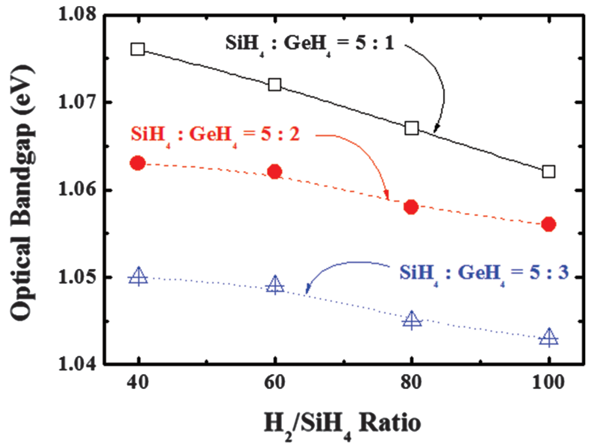

Figure 2. The optical band gap of μc-$Si_{1-x}Ge_x$:H thin films was extracted by using $(\alpha h\nu)^{1/4}$-photon energy graphs.

SiH_4/GeH_4 gas ratio was fixed at 5/1, the E_{opt} decreased from 1.076 eV to 1.062 eV for the films prepared with increasing of H_2/SiH_4 gas ratio and hence increased micro-crystallinity. And when the SiH_4/GeH_4 gas ratio was changed from 5/1 to 5/3 and H_2/SiH_4 gas ratio was fixed at 100, the E_{opt} was observed to decrease from 1.062 eV to 1.043 eV.

Figure 3 shows the Ge content within μc-$Si_{1-x}Ge_x$:H thin films, as measured by AES. The fractional Ge content within the thin film was expressed as x. Here also the x shows a nearly linear increase when hydrogen dilution was increased. With increased germane flow rates also we found an increased x. As SiH_4/GeH_4 gas ratio increased from 5/1 to 5/3, x increased, which is simply an increase in Ge content within the films from 10.8% to 17.0%, due to increased GeH_4 flow rate (at 40 hydrogen dilution). It also increased when H_2/SiH_4 ratio was increased from 40 to 100. In other words, x (Fig. 3) and X_c (Fig. 1) increased

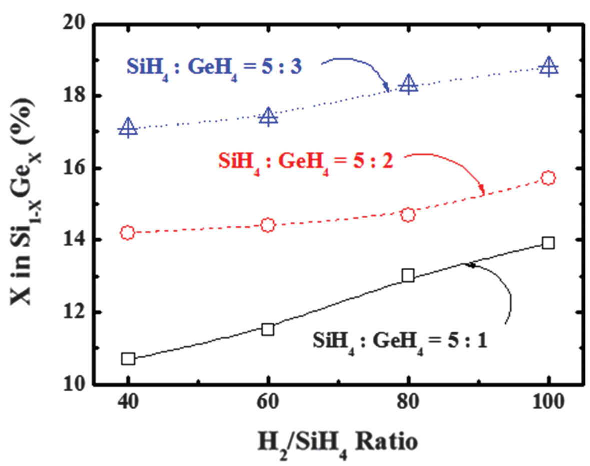

Figure 3. The Ge contents of μc-$Si_{1-x}Ge_x$:H thin films, or x, were determined by AES, for films prepared with different SiH_4/GeH_4 and H_2/SiH_4 gas ratios.

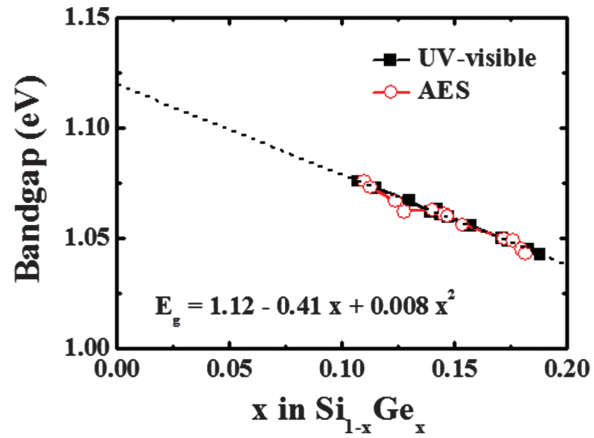

Figure 4. The correlation between Ge contents and E_{opt} in μc-$Si_{1-x}Ge_x$:H thin films using different SiH_4, GeH_4, H_2 gas flow ratios. The measured E_{opt} values were extracted form UV-vis absorption data, using Eq. (1) and the extracted E_{opt} values from AES measurements.

with the increase in H_2 flow rate,[11] whereas its optical gap decreased (Fig. 2).

Figure 4 shows the variation in optical gap of the μc-$Si_{1-x}Ge_x$:H due to the variation in x, or Ge content within the films. To find the correlation between E_{opt} and x, following equation is used.[12]

$$E_{opt} = 1.12 - 0.41x + 0.008x^2 \quad (0 < x < 0.85) \qquad (2)$$

where E_{opt} and x are the optical band gap and Ge content, respectively. The extracted E_{opt} from UV-visible (1.043 eV $< E_{opt} < 1.076$ eV) is used in Eq. (2) and x values of 0.107 to 0.188 were obtained. Using x ($0.110 < x$ of $Si_{1-x}Ge_x < 0.182$) from AES in Eq. (2), E_{opt} values of 1.045 to 1.075 eV are obtained, where the variation in x from the Eq. (2) and UV-vis measurement to that of the AES are around 3%. As the UV-vis measurement is a simpler technique as compared to the AES, so it may be possible to get some useful information of the x or Ge content of the film from the UV-vis measurement and using the method described above, that is Eq. (1) with $n = 4$ and Eq. (2).

4. CONCLUSION

We have determined a relation between the E_{opt} of μc-$Si_{1-x}Ge_x$:H and x, using a plot of $(\alpha h\nu)^{1/4}$ versus E_{ph}. The E_{opt} extracted by this method shows a lower optical gap as GeH_4 flow rate increased and H_2/SiH_4 ratio decreased. We used the comparative analysis of UV-visible and AES measurement by which some useful information related to the composition of the μc-$Si_{1-x}Ge_x$:H film can be extracted from UV-vis measurement.

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