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The influence of deposition parameters on the growth of a-SiGe:H alloys in a plasma CVD system

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Thin films of a-SiGe:H alloys were prepared by the glow discharge method from various gas mixtures of silane and germane. The effect of hydrogen dilution of the source gas mixtures on the growth and the structural, optical and electrical properties was studied. Hydrogen dilution was found to be of major importance to grow structurally dense material with highly improved photoelectrical properties, which is suitable for device application.

Hydrogen plasma etching was used to investigate the morphology of the films. SEM micrographs of the etched films demonstrate the heterogeneous network of the amorphous thin films. The alloying of a-Si:H with Ge leads to an increased microstructure, which is responsible for the deterioration of the alloy properties.

1. Introduction

Amorphous hydrogenated Si–Ge alloys have attracted much interest for various optoelectronic applications due to the possibility of adjusting their optical gap from 1.0 to 1.7 eV. However, the practical use of a-SiGe:H alloys is limited by poor photo-electrical properties, when the optical gap of the films is lowered to less than 1.5 eV. Several attempts have been made to explain the degradation of the film quality with alloying. The explanations are based upon the existence of various inhomogeneities both in the composition and the structure of the film [1–5].

The glow discharge deposition is the most common technique to produce a-Si:H based materials. Tanaka and Matsuda [6], taking into to account plasma processes and processes at the growing surface in glow discharge decomposition of silane and germane, suggested several ways to obtain high-quality a-SiGe:H alloys.

In this paper we report on the systematic study of hydrogen dilution of different SiH_4 and GeH_4 mixtures on a-SiGe:H properties in order to grow high-quality a-SiGe:H alloys with an optical gap down to 1.3 eV.

2. Experimental

Undoped a-$Si_{1-x}Ge_x$:H alloys were deposited in a capacitively coupled diode type RF glow discharge system. The RF glow discharge is confined between two parallel electrodes with an area of 120 cm^2 and a separation of 3 cm. Gas mixtures up to 20% $GeH_4/(SiH_4+GeH_4)$ were used with hydrogen dilution ranging from 0% to 95%. The total flow rate of gases was kept constant at 100 sccm, the deposition temperature was 250°C and the power density was 35 mW cm^{-2}. The total pressure in the reactor was 0.50–0.55 mbar. The films with thicknesses in the range of 0.4 to 2.0 μm were deposited on Corning 7059 glass, ITO and silicon substrates.

We used SEM micrographs to investigate the morphology of a-Si:H and a-SiGe:H films after hydrogen plasma etching. To analyze the electrical

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and optical properties we used transmission and reflectance measurements, CPM and $I-V$ characteristics. For compositional and structural analysis Fourier transformed infra-red (FTIR) spectroscopy, Rutherford back scattering (RBS) and energy dispersion X-ray (EDAX) analysis were used.

3. Results

3.1. Structure and composition

Fig. 1 shows the SEM micrographs of a-Si:H film and a-$Si_{0.5}Ge_{0.5}$:H alloy both etched in hydrogen plasma. They show that both a-Si:H and

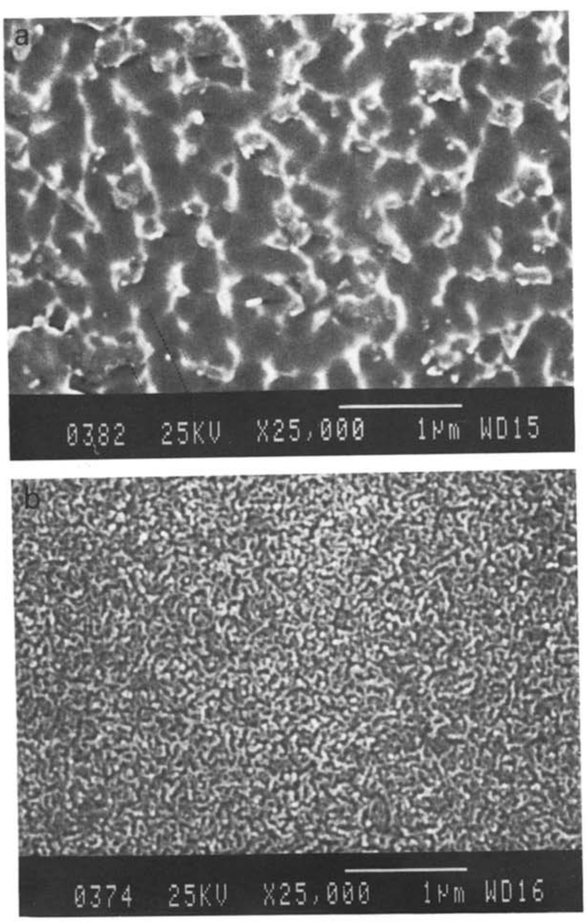

Fig. 1. SEM micrographs of (a) a-Si:H (No. 382) and (b) a-$Si_{0.5}Ge_{0.5}$:H (No. 374) films etched in hydrogen plasma.

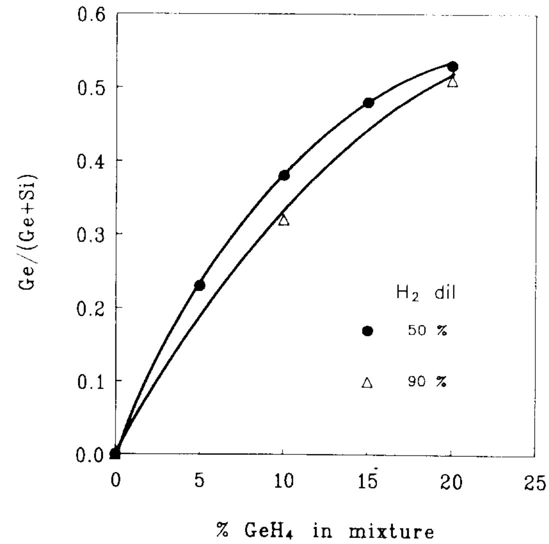

Fig. 2. Ge fraction in a-SiGe:H films versus GeH_4 fraction in $SiH_4 + GeH_4$ mixture.

a-SiGe:H films exhibit a heterogeneous network. This network is characterized by a high density part (islands or grains) and a lower density part (called tissue or grain boundary) [1,3]. The micrographs show clear difference in the size, shape and connectedness of the island and tissue components, when Ge is incorporated into the film. The increasing volume of tissue material in the a-SiGe:H alloys with higher Ge content is considered to be responsible for the deterioration of photoelectrical properties.

Fig. 2 shows the compositional ratio Ge/(Si + Ge) of the deposited a-SiGe:H films as a function of the gas ratio $GeH_4/(SiH_4 + GeH_4)$. As shown in fig. 2, the fraction of Ge atoms in the films is larger than the corresponding gaseous fraction of GeH_4 in the source gas mixture. GeH_4 is about three times more dissociative in the plasma than SiH_4, which is the cause of relatively more Ge related species reaching the growing surface. Hydrogen dilution of the source gas mixture affects the compositional ratio. We have observed that the increasing hydrogen dilution lowers the incorporation of Ge into the film, which can be explained by the strong reduction of the chemical reactivity of the growing surface [6].

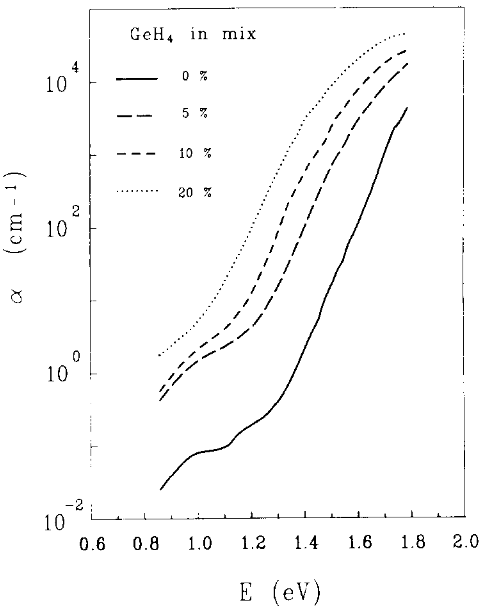

Fig. 3. Absorption coefficient of a-SiGe:H films prepared at 50% H_2 dilution versus photon energy.

3.2. Optical properties

Fig. 3 shows the optical absorption coefficient spectra as a function of photon energy for a-SiGe:H films with different Ge contents. It is clear that with an increasing Ge content in the film, the absorption increases and the absorption edge is shifted to lower energies.

The Tauc plot of the absorption coefficient versus the photon energy was used to determine the optical gap. The optical gap depends on the concentration of Ge and H in the films. H_2 dilution up to 90% has a minor effect on the optical gap. At H_2 dilution higher than 90% a remarkable increase in the optical gap is observed due to decreased Ge incorporation into the film as shown in fig. 4.

3.3. Electrical properties

The indicator that characterizes the photovoltaic quality of the material is the photosensitivity, which is the photo-to-dark conductivity (σ_{ph}/σ_d) ratio. The dark conductivity of the samples was in the range of 10^{-9}–5×10^{-8} $(\Omega\ cm)^{-1}$. The photoconductivity was measured under AM1 conditions. Fig. 5 shows the effect of H_2 dilution on the photosensitivity of a-$Si_{1-x}Ge_x$:H films. The photosensitivity in the samples with the lower Ge content ($x \simeq 0.35$) exhibits minor dependence on H_2 dilution below 90%. A strong effect of H_2

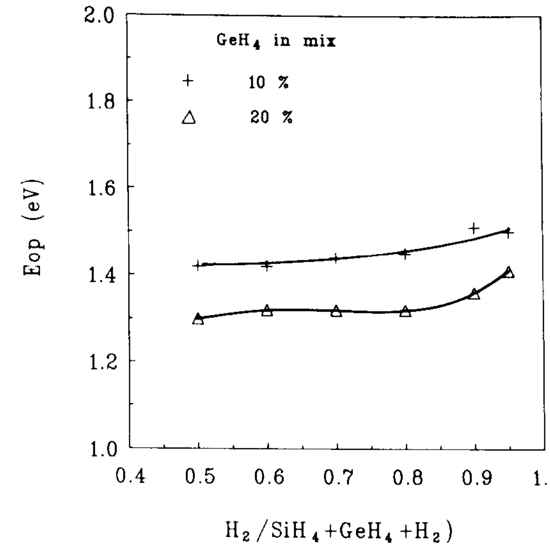

Fig. 4. Optical gap of a-SiGe:H films as a function of H_2 dilution.

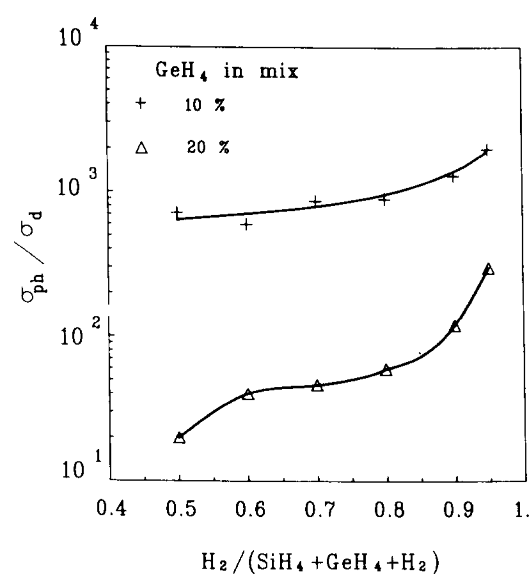

Fig. 5. Photosensitivity of a-SiGe:H films as a function of H_2 dilution.

dilution is observed for the films with Ge content around 50%, where the photosensitivity increased more than one order of magnitude. The considerable increase in photosensitivity is attributed mainly to the reduction of $Si-H_2$ related inhomogeneities, which was confirmed by IR spectroscopy analysis of the films. Sub-band gap absorption spectra obtained by CPM were used to determine the density of gap states. The observed reduction of midgap defects with the increased H_2 dilution also contributes to the higher photosensitivity.

4. Discussion and conclusions

SEM micrographs of a-Si:H and a-SiGe:H films clearly show the heterogeneous network of a-Si:H based thin films. The incorporation of Ge into the film considerably changes the structure of the film, increasing the relative volume of tissue material, which is responsible for deterioration of a-SiGe:H alloys properties.

Our results on structural and optical experiments in GD deposited a-SiGe:H films demonstrate that H_2 dilution of the source gas mixture of silane and germane plays an important role in improving the a-SiGe:H film properties. H_2 dilution minimizes the dihydride bonding and creates the conditions for growing a structurally dense network, which is in accord with the results of other groups. Strong H_2 dilution lowers the incorporation of Ge into the film by influencing both the plasma and surface chemistry which leads to the widening of the optical gap.

Using the strong H_2 dilution (90%) we prepared a-SiGe:H films with an optical gap of 1.33 eV and corresponding photosensitivity 10^2 and an optical gap of 1.4 eV and corresponding photosensitivity 7×10^2. These high-quality films are suitable for application in the back cell of tandem solar cells.

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