

a-Si_xGe_{1-x}:H thin Films

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In this work we study some optical and electronic properties of hydrogenated amorphous silicon-germanium alloys (a-Si_xGe_{1-x}:H) deposited by co-sputtering. Thin films were deposited varying silicon concentration (estimated) from 0 up-to 10 at. %. The room temperature dark conductivity changes by more than one order of magnitude with increasing silicon content, while the changes in optical properties are less expressive. The main results concerning the thin film properties, as well as the main problems related to Schottky barriers (metal/semiconductor) performance are discussed.

I. Introduction

Photovoltaic and microelectronics are two technological fields where hydrogenated amorphous semiconductors applications have grown during the years. Concerning this kind of materials, (a-Si_xGe_{1-x}:H) thin films have a special application in tandem solar cells due to the possible band-gap variation with x : from 1.04eV (a-Ge:H) up to 1.8eV (a-Si:H).

In this work, attention is directed to the $x \leq 0.1$ range mainly due to: i) our large experience in studying and working with a-Ge:H thin films^[1]; ii) the low amount of information concerning the germanium rich a-SiGe:H alloys available in the literature. The results to be shown confirm the same general behavior for the Ge rich (a-Si_xGe_{1-x}:H) alloy properties reported in ref. 2. In that reference, a noticeable increase of the photosensitivity of the samples was also observed. All these facts suggest that (a-Si_{0.1}Ge_{0.9}:H) thin films (in place of a-Ge:H) would be a better candidate for electronic applications requiring a small pseudo-gap ($E_g \leq 1.1$ eV).

Physical and technological problems related to non-intentionally doped a-SiGe:H thin films and some metal/semiconductor contacts (using Ni and Pd) are discussed in the present paper.

II. Experimental and results

The present samples were grown by rf sputtering small pieces of silicon placed over a 3" germanium target in an argon+hydrogen atmosphere. Samples with

$x=0, 0.05$ and 0.1 were grown at 220°C. Typical thin film thickness was 1 μ m. The basic employed characterizations were: NIR-VIS optical transmission (800-2500 nm), IR spectroscopy (400-4000 cm^{-1}), dark conductivity as a function of temperature (150-420 K) and photothermal deflection spectroscopy (PDS, 0.625-1.55 eV).

The silicon content in the samples was estimated using the silicon and germanium sputtering yields (for 640V Ar⁺) and the relative target areas^[2]. The total amount of bonded hydrogen was determined from the IR wagging Ge-H (565 cm^{-1}) and Si-H (640 cm^{-1}) absorption band integrated areas^[3,4]. Fig. 1 shows the IR-stretching absorption bands. Note the increase of the Si-H bulk-like mode (2000 cm^{-1}) with increasing Si content. In figure 2 it can be seen that the total amount of bonded hydrogen was almost the same (around 5.5%) in all films. It can be also observed that E_{04} (photon energy corresponding to an absorption coefficient $\alpha = 10^4\text{cm}^{-1}$) and E_{03} (same as E_{04} , for $\alpha = 10^3\text{cm}^{-1}$) experience small changes with increasing silicon content: they stayed near 1.2 and 1.0 eV, respectively. The Tauc's optical gap^[5] shows a small variation from 1.05 to 1.1 eV with increasing x .

The Urbach tail (E_u) determined from the PDS experiments are shown in figure 2. E_u is an indication of the disorder of the material^[6]. It can be seen that E_u remains approximately constant at 62meV for $x \leq 0.1$.

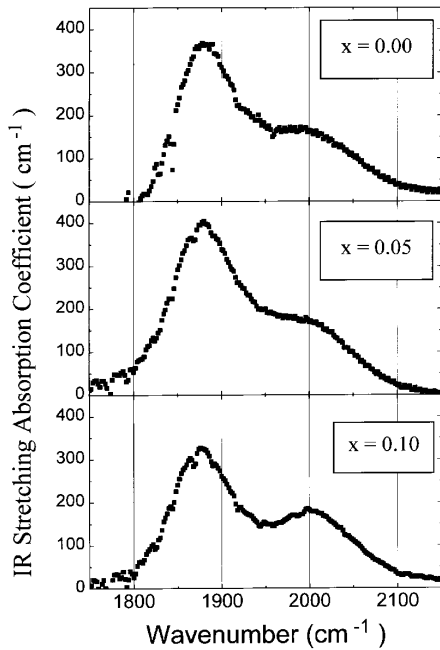


Figure 1. IR stretching absorption bands for a-Si_xGe_{1-x}:H samples with $x = 0, 0.05$ and 0.1 . The possible configurations are (see ref. 3 and 4): Ge-H bulk-like at 1880 cm^{-1} ; Ge-H surface-like at 1980 cm^{-1} ; Si-H bulk-like at 2000 cm^{-1} and Si-H surface-like at 2100 cm^{-1} . Note the increase in the 2000 cm^{-1} Si-H mode as x increases.

Nevertheless, in this figure the E_a/E_g ratio is plotted, where E_a represents the activation energy of the conductivity measurements and E_g , the Tauc's optical gap. It can be observed that E_a/E_g varies from 0.44 up to almost 0.5, what indicates that the chemical potential (or the Fermi level, in an abuse of nomenclature) has been displaced toward the center of the material's gap. Still considering the dark conductivity measurements, in figure 3 it can be verified that with increasing silicon content, a change of more than one order of magnitude is achieved (for $x = 0$ up-to 0.1) at room temperature, the sample being more resistive. This effect is more pronounced at low temperatures. In ref. 2 it is also shown that with increasing amount of silicon in the film the transport properties have more expressive changes than the optical ones.

In order to study the possible rectifying properties of a-SiGe:H/metal interfaces, the following device structure were deposited: using a Corning Glass 7059 substrate, 3000 \AA of Cr is sputter deposited. Then, a small area is protected (from further depositions) to serve as one probe contact. After that, without opening the deposition chamber, another metal layer (Ni and Pd) is deposited. The next layer was 5000 \AA of a-Si_{0.1}Ge_{0.9}:H,

followed by a 300 \AA a-SiGe layer. Chromium dot contacts (0.5 mm diameter) were deposited as a last step. The a-SiGe layer between the a-SiGe:H and Cr dot contacts is used to provide an ohmic contact at this side of the device. The behavior of a non-stable diode is shown in figure 4 and is discussed in the next section.

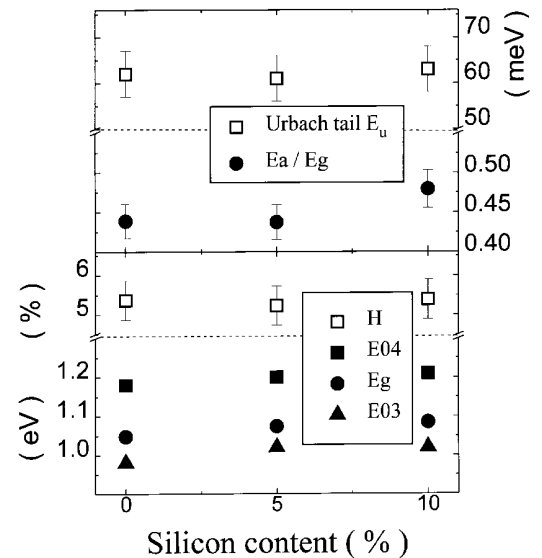


Figure 2. Up: Urbach tail E_u and E_a/E_g ratio (E_a represents the activation energy of the dark conductivity measurements and E_g is the Tauc's optical gap). Down: Total amount of bonded hydrogen H (%), Tauc's optical gap E_g (eV) and E_{04} , E_{03} (see text).

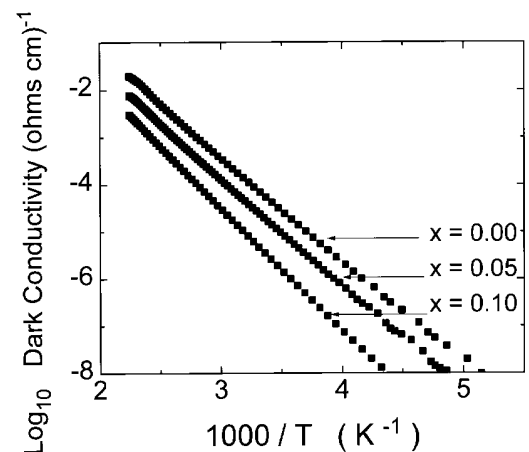


Figure 3. Dark conductivity as a function of temperature. Note the increment in resistivity with increasing silicon content.

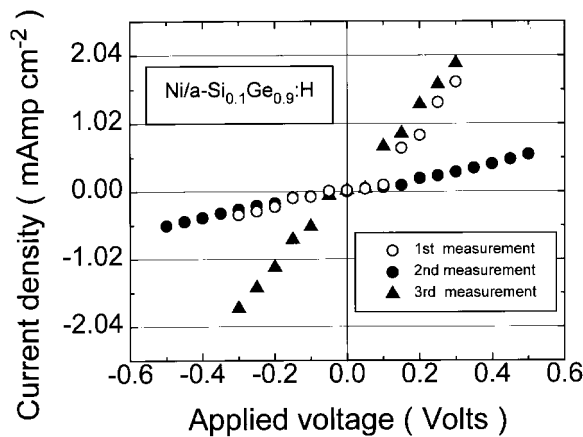


Figure 4. Non-stable behavior of I vs V characteristic of a Ni/a-SiGe:H contact. The three different measurements were done on the same diode.

III. Discussion

Consider a-Ge:H as the starting material. The introduction of Si into the Ge amorphous matrix can produce several changes in film properties, many of them being completely unforeseen. The sp^3 orbitals are split by the bonding interactions to form the valence and conduction bands. The splitting between the bonding and anti-bonding states is larger in Si than in Ge, a fact that leads to increased energy gap as a function of Si content. This last effect is not so strong for $x \leq 0.1$.

The electronic density of states (DOS)^[7] of amorphous semiconductors can be described by: i) tails of localised states near the band edges originated from disorder and ii) coordination defects (dangling bonds, DB) deep in the pseudo-gap. According to the PDS measurements, the Urbach tail E_u did not change for $x = 0$ up-to 0.1. Nevertheless, the transport properties were severely influenced, what can be explained by variations in DB density and energy distribution and/or variations in carriers mobility. The first argument seems to be more plausible due to the preferential attachment of H to Si (than to Ge): the hydrogen located near two Si and Ge atoms would preferentially attach to Si^[8]. This would reduce the Si DB contribution to the DOS. It seems to be confirmed by ESR measurements^[9] where, even for an a-Si_{0.42}Ge_{0.58}:H alloy, the Ge DB seem to dominate.

Considering the metal/semiconductor interface, reasonable rectifying properties were not found up to the moment, as can be seen in the open circle plot of figure

4 (this figure represents an Ni/a-Si_{0.1}Ge_{0.9}:H diode). This might be explained by the existence of a large density of deep states in the amorphous alloy pseudo-gap, what may produce tunnelling transport through the barrier. In addition, a more critical effect would be the existence of structural defects like bubbles and pin-holes that may produce parallel conduction paths and short-circuits. Non-stable behavior was also observed: it is not possible to know when a diode will be damaged (short-circuited or will become a simple series resistance^[10]). Nevertheless, (even for Pd contacts) the same behavior of figure 4 was always found: before becoming a simple (low value) resistance (up-solid triangles), every diode loses its rectifying properties (solid circles). At this step, the forward and reverse polarizations are completely symmetric and the main change is due to the increased forward resistivity. Annealing at 180°C for 30 minutes did not improve the rectifying properties, although it was observed a complete elimination of existing short-circuits. The general non-stable behavior is not completely understood and is under study.

IV. Conclusions

In this work we have studied some a-Si_xGe_{1-x}:H (Ge rich) thin film properties. It was shown that the inclusion of small ($x \leq 0.1$) silicon content in the Ge amorphous matrix produces small optical properties variations. Large changes are observed in the transport properties where the chemical potential seems to be displaced toward the center of the material gap, and changes of more than one order of magnitude were observed in the dark conductivity at room temperature.

Non-stability was found in metal/a-Si_{0.1}Ge_{0.9}:H interfaces, using both Ni and Pd. There can exist two main problems related to non-rectifying behavior: i) the high density of states in the material gap, which can provide a path for tunnelling conduction; ii) the existence of pin-holes in the amorphous matrix, which can provide a short-circuit path. Further works are on development to clarify the point, and to improve the metal/semiconductor barrier performance.

Acknowledgements

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