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Low temperature stress-induced crystallization of germanium on plastic

D. Shahrjerdi, B. Hekmatshoar, L. Rezaee, S.S. Mohajerzadeh*

Thin Film Laboratory, Department of Electrical and Computer Engineering, University of Tehran, Tehran, Iran

Abstract

Crystallization of a-Ge was performed on flexible plastic substrates at temperatures as low as 130 °C. Copper has been primarily used as the seed of crystallization, while an external stress was applied onto the flexible substrate to enhance the crystallization. The substrates used for this study were mainly 0.1 mm thick Polyethylene terephthalate (PET) films, which remain flexible during post treatment at low temperatures. Various samples were subject to tensile or compressive stress for the annealing step. It has been observed that only in the case of a compressive stress, crystallization becomes possible. A final electrical sheet resistance of less than 45 kΩ/□ is achieved after an annealing period of 3 h. XRD, SEM and Hall mobility measurement have been exploited to study the crystallization and explain the drastic drop of electrical resistance in samples subjected to external compressive stress. The ⟨2 2 0⟩ peak of Ge is discernible in the XRD spectra, confirming the crystallization. Also the study of surface morphology using SEM corroborates the crystalline nature of the annealed Ge film and the evolution of cracks. A carrier mobility of more than 110 $cm^2/V\,s$ is observed for holes using Hall measurement. The shrinkage of PET during annealing induces compressive stress both in the substrate and the over-layer, in addition to the externally applied stress. This causes the progressive evolution of cracks in the Ge layer and a weak interfacial buckling of the Ge film.

Keywords: External stress; Compressive stress; Low temperature crystallization; Flexible substrates; Polycrystalline germanium

1. Introduction

Stress-induced crystallization is a well-known phenomenon in polymers [1,2]. Effects of compressive and tensile external stress on the crystallinity of polymers and the improvement or degradation of their quality have been widely investigated [3]. Interfacial stress-induced crystallization of polyethylene composites and internal stresses that involve the adhesion of SiO_x coatings on Polyethylene terephthalate (PET) have been recently examined [4,5]. On the other hand, crystallization of amorphous semiconductors such as silicon and germanium is commonly performed by metal induced crystallization techniques [5–7]. These methods reduce the temperature of crystallization dramatically, although the annealing temperature is still too high for plastic substrates. Also metal contamination is a serious concern in such techniques.

Attempts have been made to suppress the deleterious effect of metal contamination using a metal-induced lateral crystallization or MILC [8,9]. MILC, however requires annealing temperatures higher than metal-induced crystallization. There seems to be an inevitable trade off between low metal contamination and processing temperature leading to temperatures more than 200 °C for germanium crystallization [10–13]. Further reduction of temperature is believed to need additional ingredients in the annealing process to supply the required activation energy. Study of the effects of internal and external stress has recently opened a new scope in the field of semiconductor materials and devices, especially when the interfacial effects of the layer and substrate are concerned. The intrinsic compressive stress, primarily induced during the growth of thin hydrogenated amorphous silicon layers on a substrate, has been studied and the resulting properties have been investigated by bending or flexural oscillation [14]. External stress in the metal oxide semiconductor structure and the impact of tensile stress on current–voltage characteristics of such devices have been examined in Ref. [15], showing degradation in the electrical properties for such structures.

In the present work, we report for the first time, a stress-induced crystallization technique to grow polycrystalline germanium on plastic substrates at tempera-

*Corresponding author. Tel./fax: +98-21-801-1235.
E-mail address:
smohajer@sun1.vlsi.uwaterloo.ca (S.S. Mohajerzadeh).

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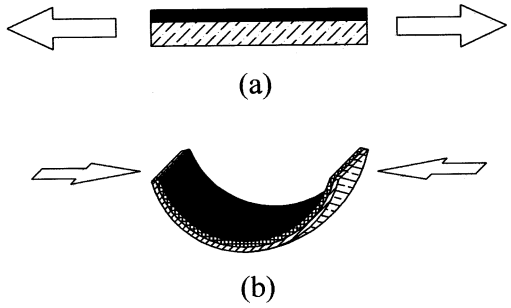

Fig. 1. Schematic setup used for this study. The tensile stress is accomplished by means of stretching the sample outward (a); whereas the compressive stress is applied bending the sample inward (b).

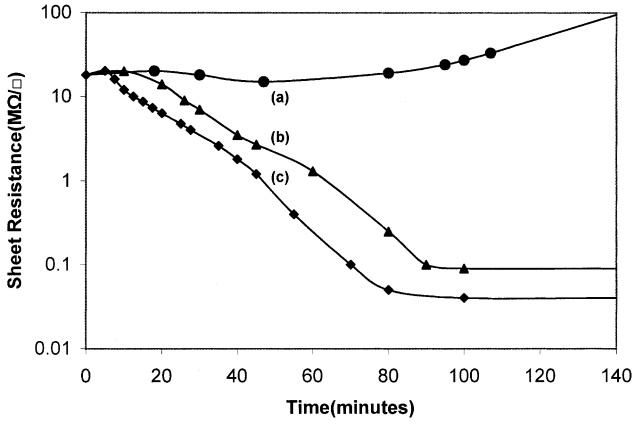

Fig. 2. The results of electrical sheet resistance scanning with respect to time for three different annealing methods, (a) sample under tensile stress; (b) sample without external stress and (c) sample under compressive stress. A considerable reduction in the electrical sheet resistance is an indication of better crystallinity of the sample prepared using this method.

tures as low as 130 °C. The effect of external stress, either tensile or compressive, is studied. Films with high carrier mobility are fabricated using an external compressive stress. Also the evolution of cracks, as a detrimental event is addressed and a suggestion to minimize this negative effect is proposed.

2. Experimental

One hundred micrometer films of PET were employed as flexible substrates. The cleaning sequence of the substrates consists of washing the PET samples with D.I. water, exposure to chemical solvents and further washing in a RCA#1 solution, rinsing in D.I. water and finally drying using air-blow. The heat distortion temperature of PET is 225 °C, but its maximum temperature of use is 180 °C and it is observed that annealing temperatures above 180 °C severely deform the plastic. After cleaning, the samples are placed in the deposition chamber at a distance far away from the evaporation sources to avoid excessive heating of the plastic, causing severe damage.

After loading the samples into the chamber and achieving a base pressure of 2×10^{-6} Torr, samples are maintained at a temperature of 100 °C for film deposition. A Ge charge with 99.999% purity was used as the source of germanium evaporation. Five hundred Angstrom of Ge was e-beam deposited, followed by thermal deposition of a 10–15 Å copper layer, and a consecutive 500 Å Ge over-layer. The thickness of the films is monitored using a standard quartz crystal microbalance. After unloading the samples, post thermal treatment is carried out at temperatures ranging from 130 to 180 °C. Two different types of external mechanical stress were applied to the substrate during annealing by bending the substrate inward for a compressive stress, or stretching for a tensile one (Fig. 1).

3. Results and discussion

The change of the electrical resistance of the germanium layer has been continuously monitored during the post thermal treatment and the corresponding traces have been collected in Fig. 2. For this study, the annealing was performed at a temperature of 150 °C. The initial sheet resistance of all the samples was approximately 18 MΩ/□. The curves in this figure show the variation in the electrical sheet resistance with respect to the annealing time for three samples, two of which were subjected to compressive and tensile stress. The third curve represents the data for the sample with no external stress during thermal treatment. All three samples experience an initial increase of their resistance to values of approximately 20 MΩ/□. This minor increase is believed to be primarily due to diffusion of Cu into the Ge layer. After this initial increase, the resistance of all the samples starts to drop to smaller values. When no external stress is applied, the sheet resistance drops to 4.5 MΩ/□ and then it rises very slightly. For a tensile stress the resistance shows a minor reduction and a considerable increase to values as high as 300 MΩ/□. In the case of a compressive stress, the

Table 1
Final whole mobility and electrical sheet resistance for samples of Fig. 1

Condition	Before annealing	No stress	Compressive stress	Tensile stress
Mobility	2.8–3.9 $cm^2/V\,s$	4.2–5.9 $cm^2/V\,s$	100–110 $cm^2/V\,s$	Nearly zero
Resistance	17 MΩ/□	4.8 MΩ/□	45 kΩ/□	⩾300 MΩ/□

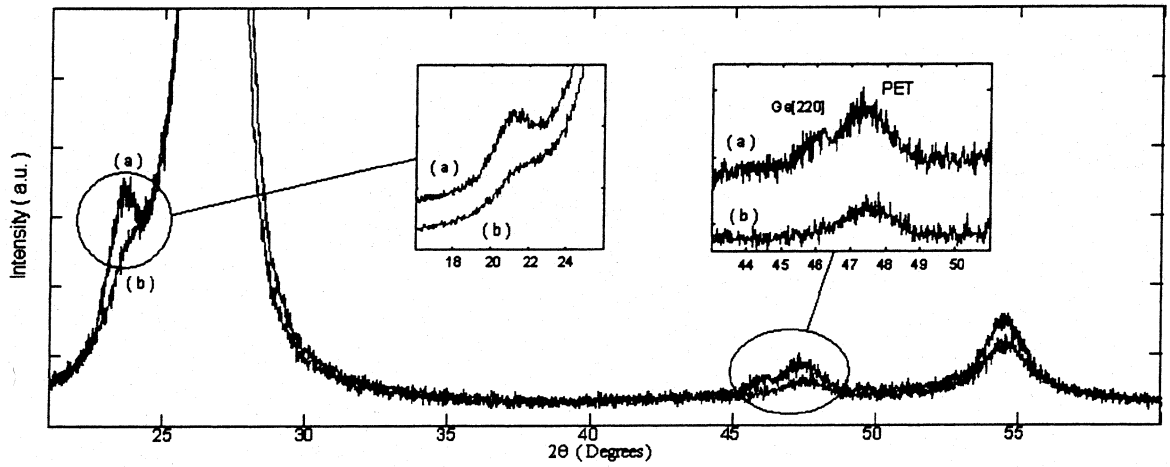

Fig. 3. The result of XRD spectroscopy with (a) a compressive stress and (b) with no external stress. The ⟨2 2 0⟩ peak of Ge is discernible in the insert of this figure. Also ⟨1 1 1⟩ orientation of tetragonal structure of Ge is seen in the insert in the left hand side of the figure.

electrical resistance exhibits a monotonic decrease by about three orders of magnitude to 45 kΩ/□. This enhancement of the film conductivity is believed to be due to an improvement in the crystallinity of the germanium layer.

Hall mobility measurements have also been performed for the samples of Fig. 1 and the results are summarized in Table 1. Final electrical sheet resistance is also given for better comparison. The data in this table evidences a close relationship between the final electrical resistance and the measured carrier mobility. An improvement in the mobility from a value of 3 to 4 $cm^2/V\,s$ for the sample without heat treatment to a value of 110 $cm^2/V\,s$ for the sample with a compressive stress indicates a dramatic enhancement in the crystallinity of the films during such a thermal treatment. The mobility is not measurable for samples subjected to tensile stress. The electrical observations imply that by applying an external stress, germanium film is crystallized and compressive stress enhances this process.

The crystallinity of the samples has been studied using XRD analyses. X-ray diffraction spectra are col-

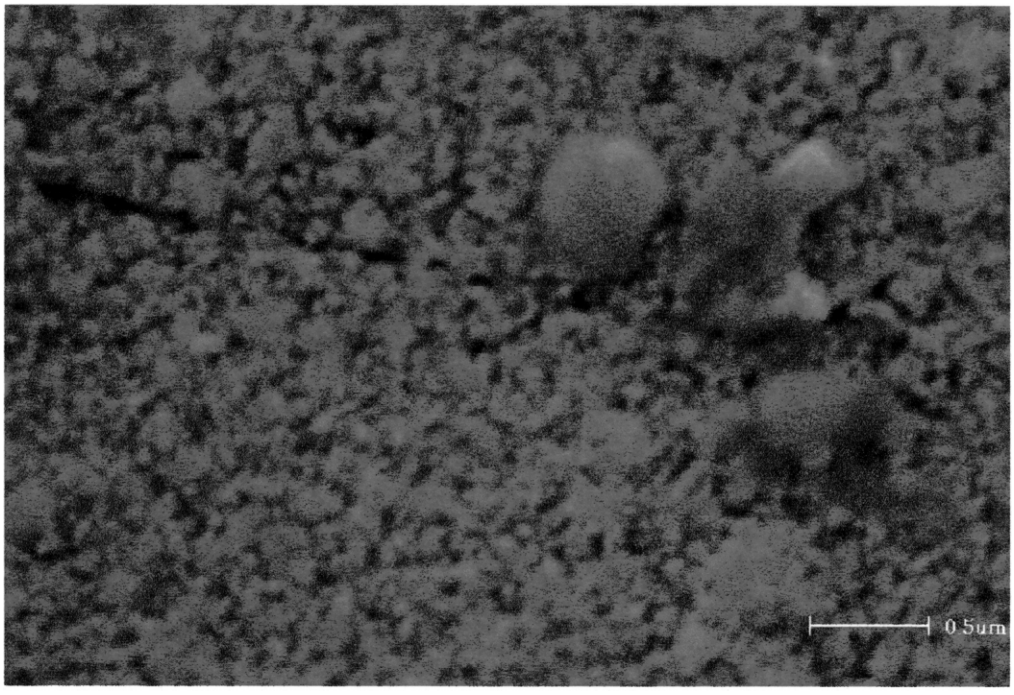

Fig. 4. The result of SEM microscopy on the sample prepared using external compressive stress evidencing the crystallization of Ge layer.

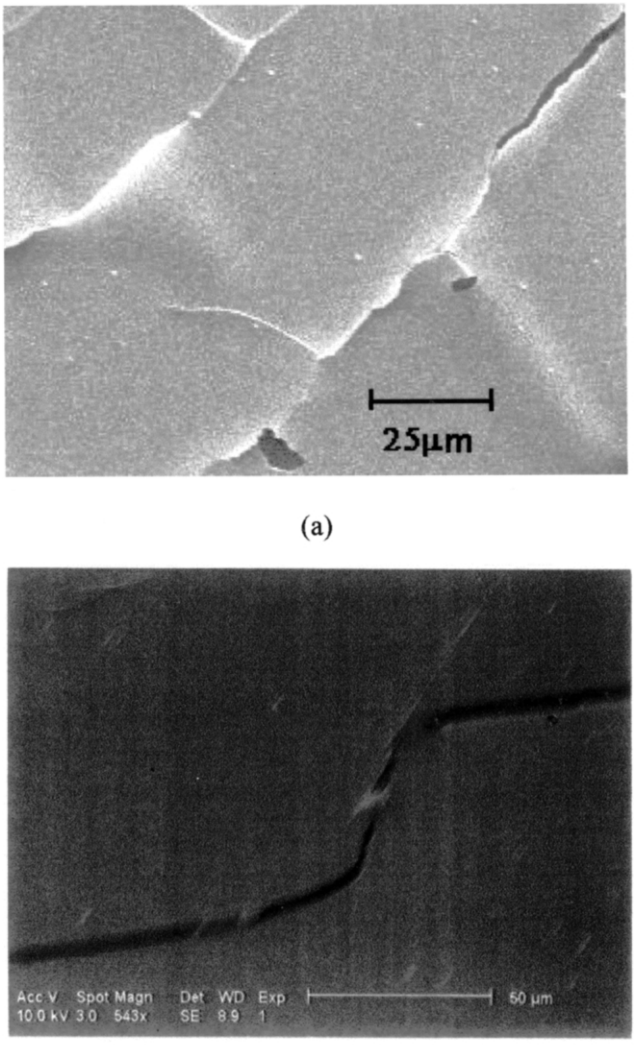

Fig. 5. (a) Evolution of cracks in the Ge layer for the sample under compressive stress. The buckling of Ge film is observed in this image; (b) Crack formation in the sample prepared with a tensile stress showing a large crack in both PET and Ge layer.

lected in Fig. 3 for the sample subjected to compressive stress and the one treated without stress during thermal annealing. PET is partially crystalline and its spectrum exhibits a large peak at values of 26.1° and two other peaks at 46.8 and 53.6°, respectively. The insert in this figure shows the evolution of the Ge ⟨2 2 0⟩ peak at 45.2° which is quite discernible for the sample annealed in the presence of an external compressive stress. It must be born in mind that the film thickness is less than 0.1 μm and the diffracted signals from such a thin film are buried in the peaks from the partially crystalline PET substrate. Also in this figure one can see a peak at 22.8° which could be due to ⟨1 1 1⟩ orientation of germanium from a tetragonal structure. The XRD results also indicate the evolution of a polycrystalline Ge layer due to the applied compressive stress.

The surface morphology of the sample annealed in the presence of external compressive stress has been studied by SEM analysis and is depicted in Fig. 4. The sample annealed without stress has a smooth surface, not presented here. The sample has been exposed to NH_4OH for 15 s to develop surface features. Fine grains of polycrystalline Ge are randomly distributed on the surface with an average grain size of approximately 0.1–0.2 μm in diameter. Also grains with sizes up to 0.5 μm are observed in this image.

Evolution of cracks is an important phenomenon whenever strained thin films are concerned [16]. Fig. 5 shows the surface morphology of cracks taken by SEM for the samples subjected to compressive and tensile stress, respectively. In Fig. 5a, one can see that parallel cracks of Ge are observed at approximately 50 μm separations from each other. Also in this figure buckling of the germanium film is observed which is believed to be mainly due to the compressive stress. The evolution of parallel longitudinal cracks needs further study before a conclusion can be reached. It has been claimed that parallel cracks of coatings on polymer substrates are resulted by the tensile stress that the coating itself exerts onto the substrate to oppose the shrinkage of polymer during annealing [17]. In Fig. 5b the SEM morphology of the sample subjected to a tensile stress is displayed. As seen in this image, no surface feature is evident for the germanium layer except for a deep and wide crack in the upper layer which can be due to substrate stretching during thermal treatment. Accumulation of these cracks seems to account for the sudden increase of sheet resistance in the case of tensile stress.

Although buckling does not affect the electrical continuity of the Ge layer until the layer is peeled off, it seems to hamper device fabrication, especially if another layer is going to be deposited on Ge. One of the previous works [5] proposes that compressive stress is reduced if the thickness of the coating is increased; so it can be anticipated that the buckling effect would also be reduced. This might have the drawback of degradation both in the rate and quality of crystallization, since internal compressive stress has a drastic effect on the crystallization phenomenon. We believe that both the longitudinal and transverse deformations would be suppressed if patterned structures were used. We have also observed that by lowering the temperatures below 130 °C, crystallization is hindered. On the other hand, annealing at temperatures higher than 180 °C will cause PET to damage severely.

Metal contamination of the Ge layer will be another concern for device fabrication. Cu incorporation can be minimized by depositing a minimal thickness of Cu required for crystallization. However, metal contamination cannot be totally eliminated, as it was verified that

a minimum level of copper is necessary to make the crystallization process feasible.

4. Summary and conclusion

In summary, Cu-assisted stress-induced crystallization of a-Ge has been presented and effects of external stress and especially the compressive one, have been discussed and verified by XRD, SEM and Hall mobility measurements. A final whole mobility of 110 $cm^2/V\,s$ and electrical sheet resistance of 45 $k\Omega/\square$ have been obtained for the samples annealed at 150 °C in the presence of an external compressive stress. This method suggests that a considerable reduction of crystallization temperature can be achieved if a proper stress is applied during post treatment. The evolution of cracks in the germanium layer hampers the fabrication of electrical devices and must be minimized. We believe that by using properly patterned structures, one can reduce such a deleterious event. The crystallized germanium layers have been used for the fabrication of thermocouple arrays on PET as will be published elsewhere. This technique is being extended to examine possible crystallization of alloys of germanium and silicon films and their application in realizing thin film transistors on PET.

Acknowledgments

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