Fabrication of Poly-Ge-Based Thermopiles on Plastic

Bahareh Sadeghi Makki, Maryam Moradi, Ali Moafi, Shams Mohajerzadeh, Bahman Hekmatshoar, and Davood Shahrjerdi

***Abstract*—Fabrication of Ge-based thermocouple on polyethylene-terephthalate (PET) plastic substrates is reported. The amorphous Ge film, deposited using electron beam evaporation, is post treated to form a polycrystalline film. The annealing process has been performed at temperatures ranging from 120 °C to 175 °C and study of physical characteristics of Ge films using XRD and SEM confirms its crystallinity. A value of 100 μV/°C is extracted for the Ge-Al junctions. The thermocouple fabrication and its response to flow are reported. A novel approach is described to perform the micromachining of PET substrates for the formation of craters and membranes. Di-methyl-formamide (DMF) is used as the solvent of the PET substrate, masked with a Ge/Cu multilayer. An average chemical etch rate of 12 μm/h is achieved in the presence of 6.5 mW/cm^2 of 360-nm UV at ambient temperature.**

***Index Terms*—Flexible substrates, Ge thermocouples, micromachining, polyethylene-terephthalate (PET) etching, ultraviolet illumination.**

I. Introduction

THERMOCOUPLE devices are, by far, the most frequently used sensing elements in many applications [1]. Their usage ranges from realization of simple temperature monitoring devices to biosensors and infrared detectors [2], [3]. Despite diversity in its applications, the essence of the devices lays on the Seebeck effect, where slight variations in temperature yield the developing of a measurable voltage across the junction. Arrays of thermocouples, known as thermopiles, are most frequently used in realizing miniaturized sensors. In such devices, the thermocouple junction is placed in such a way that the overall voltage will be the sum of all individual voltages across each junction. Silicon-based thermopiles are regularly used in realizing many devices such as pressure sensors [4], flow meters [5], etc. [6], [7]. In the case of polysilicon-based devices, the processing temperature exceeds 600 °C, where many substrates cannot withstand. Metallic-based devices require much lower temperatures during processing and fabrication of thermocouples can be achieved on thin rubber membranes and flexible bases [8]. The low sensitivity of the junction, however, makes the readout circuitry more complex. Germanium, on the other hand, can be processed at temperatures far below that of silicon and the junction sensitivity remains high. Alloys of Si-Ge are suitable candidates for making high-performance thermocouple-based devices [9].

In this paper, we report the successful fabrication of Ge-Al thermocouples at processing temperatures lower than 175 °C. The formation of polycrystalline-Ge is achieved using Cu-induced crystallization in the presence of an external compressive stress. In addition, a novel ultraviolet-induced anisotropic etching of polyethylene-terephthalate (PET) plastics is reported to form 80-μm-deep craters and membranes. Strong solvents, like DMF and DCM, were used to etch PET in the presence of ultraviolet exposure. A bilayer of Ge-Cu is exploited as the mask for the etching process. Evolution of cracks in the mask hampers long time etching and must be minimized. In addition, sharp edges are formed in the presence of ultraviolet illumination in the opening areas. In the following sections, a description of experimental setup used for this investigation is given. Then, the results of physical and electrical characterization of polycrystalline Ge films and Ge/Al thermocouples are presented. Micromachining of plastic in the presence of ultraviolet illumination is described in the last section. A completed device on a 30-μm-thick membrane is illustrated.

II. Fabrication

Flexible PET is used as the substrate for the fabrication process. A sandwich of 0.1-μm Ge, 50-Å Cu, and 0.1-μm Ge makes the main constituent of the process. Aluminum is the other component for the flexible thermopiles. Ge and Al arms with 20-μm width and 1-mm length form arrays of three to ten thermocouples in a series. All depositions are carried out in a vacuum chamber at a temperature of 110 °C with a base pressure of 1×10^{-6} torr. Since the as-deposited Ge layer is amorphous, a metal-induced crystallization technique is employed to form polycrystalline films. During this post-treatment step, the flexible substrate is subjected to compressive and tensile strain at temperatures as low as 135 °C to enhance crystallinity at reduced temperatures. External strain seems to reduce the annealing temperature allowing fabrication on plastic.

The crystallization has been confirmed using XRD and SEM analyses. The XRD spectra reveal the partial crystallinity of the PET as well as $\langle 220 \rangle$ orientation of the poly-Ge layer, as seen in

Manuscript received October 31, 2002; revised December 14, 2003. This work was supported in part by a grant from the Center of Excellence of Applied Electromagnetics, University of Tehran, Iran, in part by a grant from the Ministry of Industry, and in part by the Faculty of Engineering, University of Tehran. The associate editor coordinating the review of this paper and approving it for publication was Dr. Chang Liu.

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Digital Object Identifier 10.1109/JSEN.2004.836862

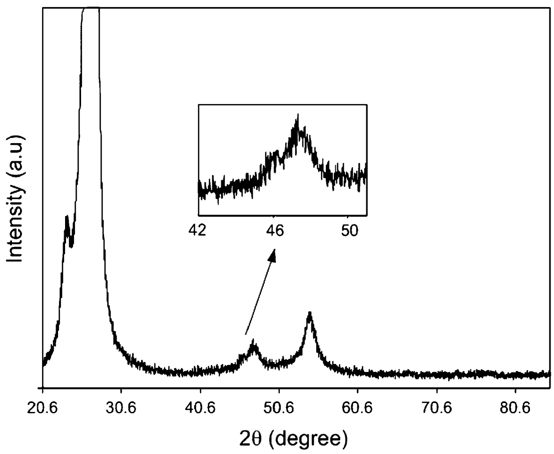


Fig. 1. XRD crystallography of Ge on PET. The ⟨220⟩-Ge peak is discernible in the PET spectra.

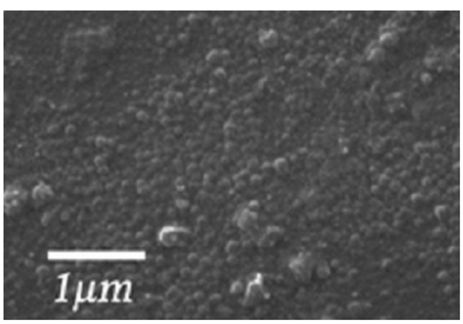


Fig. 2. SEM surface morphology of Ge after 30-s exposure to NH_4OH for feature development. A grain size of 0.5 μm is observed for the Ge layer.

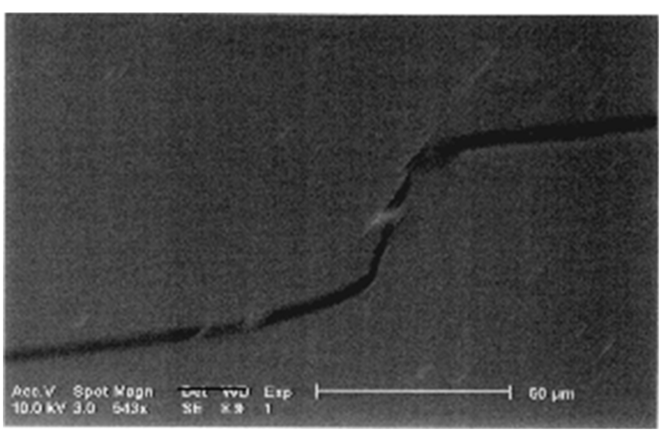
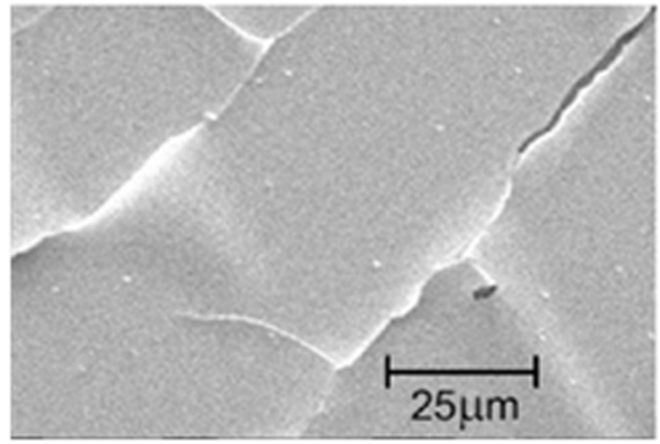


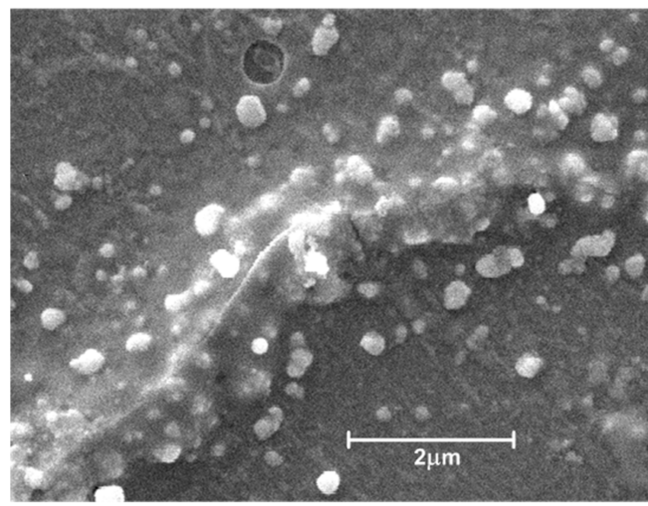
Fig. 3. SEM morphology of Ge on PET indicating crack formed during thermal annealing with tensile stress.

Fig. 1. The large peaks in the spectra belong to PET itself, and the ⟨111⟩ Ge peaks are buried in the PET spectrum. However, as seen in the inset of Fig. 1, the ⟨220⟩ orientation is quite discernible. SEM was used to study the sample morphology after 30-s immersion in an NH_4OH solution to develop crystalline features. The image given in Fig. 2 clearly shows the granular structure of the Ge film, indicating its crystalline nature.

One of the major concerns when dealing with plastic substrates is the evolution of cracks in the Ge layer, which could be a result of thermal expansion of the substrate. Fig. 3 presents the



(a)



(b)

Fig. 4. (a) SEM micrograph for the sample treated under a compressive stress indicating buckling of the Ge layer with 50-μm separation and in the form of parallel lines. (b) Closer view on the sample at the vicinity of a buckled site. The grains are larger as a result of higher stress accumulated in this area.

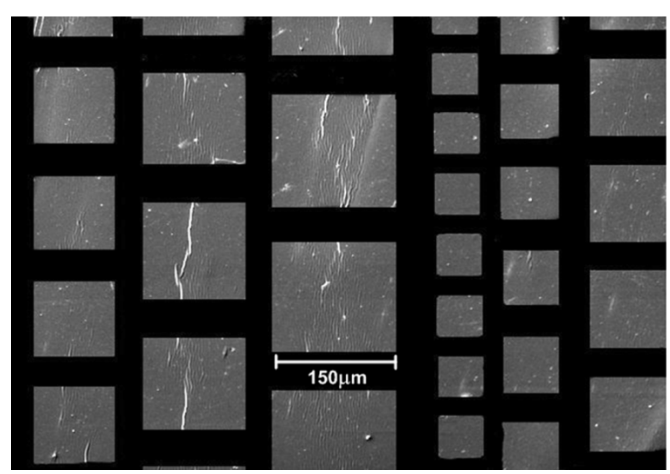


Fig. 5. Minimizing crack formation by using patterned structures. Squares with 100-μm sides do not show any crack, whereas those with larger dimensions are defective.

SEM micrograph of the Ge layer, ruptured by a large crack. This sample has been subjected to an external tensile stress during

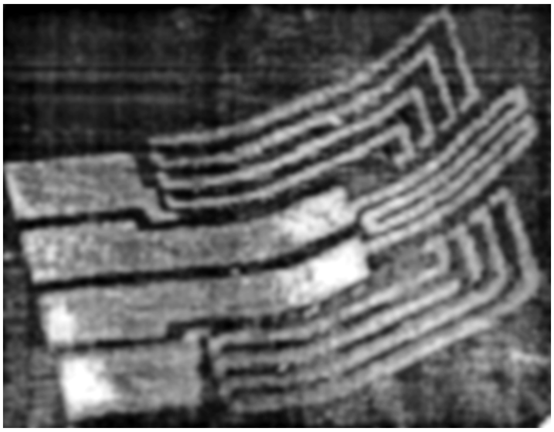


Fig. 6. Fabricated Ge-based thermocouple on PET under intentional bent to indicate its flexibility.

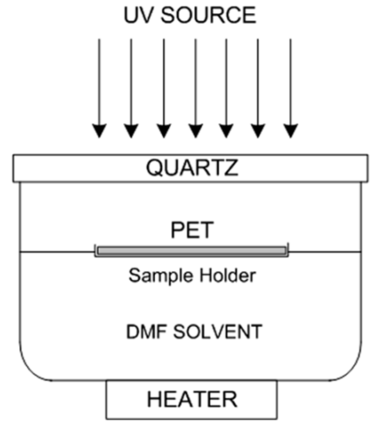


Fig. 9. Setup used for PET etching in DMF under UV exposure. Temperature of solvent must be kept around 115 °C during etching for a considerable rate.

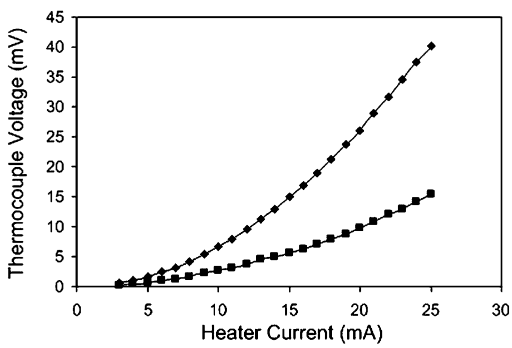


Fig. 7. Comparison between sensitivity of (a) Cr-Ni and (b) Ge-based thermocouples, showing improved response of the latter case.

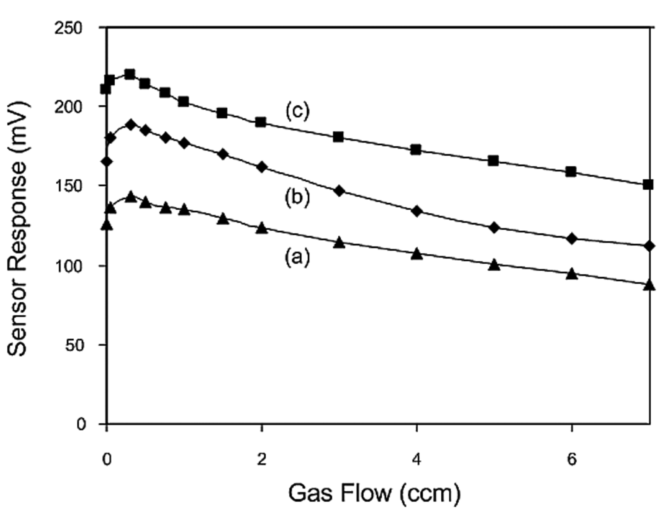


Fig. 8. Sensor's response to gas flows at three heater currents of (a) 10, (b) 15, and (c) 20 mA, respectively.

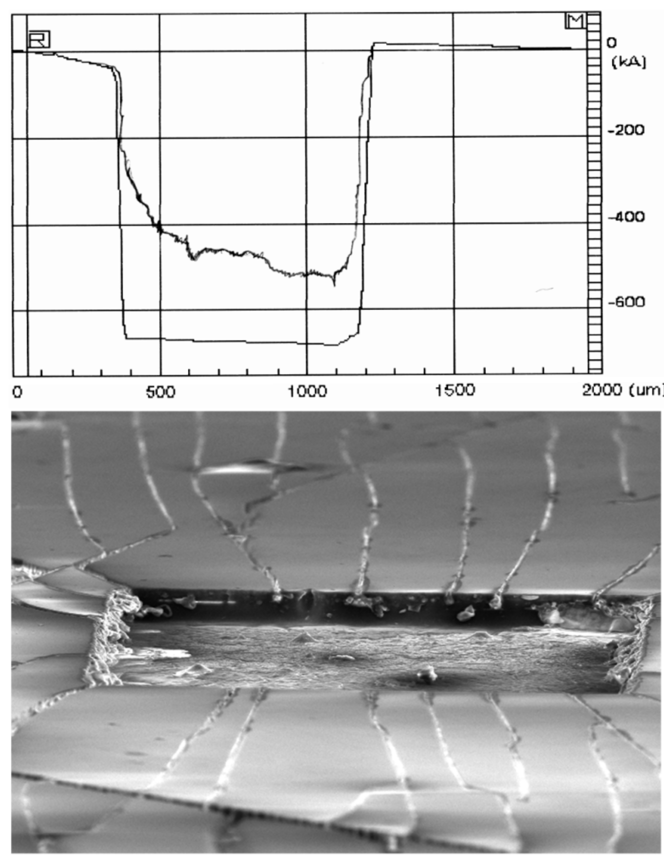


Fig. 10. Generation of a 40-μm-deep crater in PET after etching in DCM under UV exposure (bottom image). Streaks on the surface are due to cracks in the mask. The figure on top shows the results of depth measurement using a Dek-Tak3 stylus profilometer. The rough surface of the crater is the result of DCM aggressive etching of PET. By using pure DMF, a smooth surface with a considerably higher etch rate is achieved.

thermal treatment at a temperature of 150 °C. By using an external compressive stress, on the other hand, cracks take the form of buckling, as seen in Fig. 4(a). The buckling sites are in parallel lines with 50-μm separation. The accumulation of stress at these sites leads to a significantly improved crystallization, as observed from SEM morphology examination. Fig. 4(b) depicts a close view of the sample treated under a compressive stress with the granular structure at the area in the vicinity of buckling sites. The formation of cracks in its rupture or buckling forms must be diminished before a reliable device can be fabricated. Patterning the Ge layer before thermomechanical treatment has circumvented this problem. Fig. 5 presents an SEM image of the surface morphology of the sample treated with a compressive stress equivalent to the previous sample but with

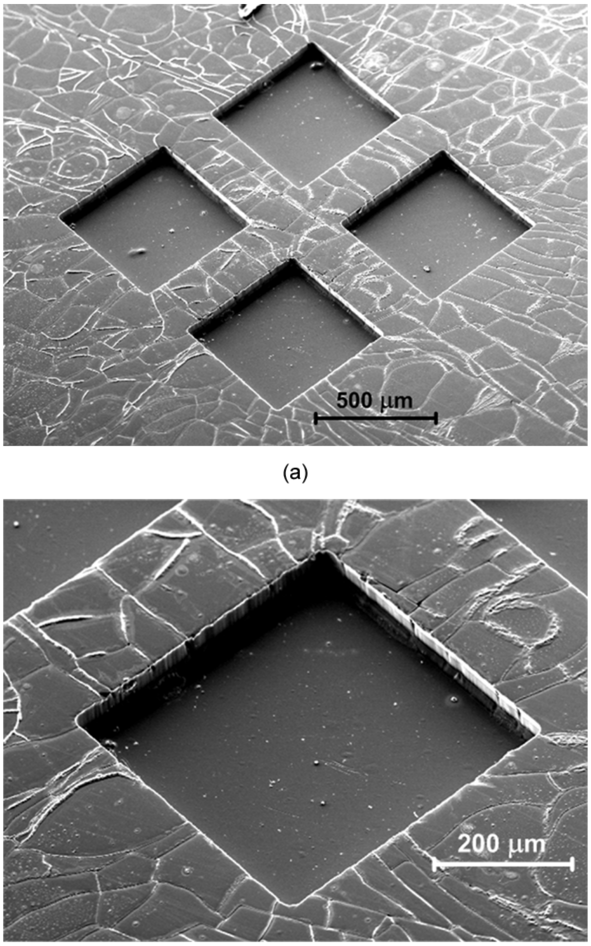


Fig. 11. (a) SEM micrograph of the sample etched in DMF solution in the presence of ultraviolet illumination and with a solution temperature maintained at 115 °C. Streaks in this figure are not deep and do not cause severe damage in the structure. (b) Higher magnification view of the sample in part (a) showing a sharp and well-defined edge.

patterned structures. Squares with a 100-μm length, do not experience crack formation, whereas the larger structures show a distinguishable crack, mainly at the center of the square.

The electrical conductivity of the annealed sample has been monitored during the thermomechanical treatment period, showing a 1000× increase in value compared to that of a Ge layer. This dramatic increase in electrical conductivity seems to be due to an improvement in the carrier mobility, further corroborating the crystalline nature of the Ge layer after post treatment. A value of 100 cm^2/Vs is extracted for the hole mobility from Hall measurements.

The crystallized Ge has been employed in realizing thermocouple arrays on PET using Al as the other arm. Fig. 6 shows a completed thermocouple-based gas flow sensor on PET under an intentional bent to show its flexibility. Al seems to be suitable for this flexible thermocouple array and a Seebeck factor of 100 μV/°C is extracted for the Ge-Al junction. The fabricated devices have been compared with Cr-Ni thermocouples made on glass substrates. Although Cr and Ni could be used as the other arm for such thermocouples, the cracks in the metallic part severely hamper their application on PET. In Fig. 7, the sensor response to electric currents in the Cr-made heater is compared for Cr-Ni and Ge-based thermocouples, indicating the superiority of Ge-Al thermocouples over Cr-Ni ones. By increasing the current through the heater, the voltage developed across the junction increases. In the case of Ge-based devices, a significant improvement is observed in sensor response mainly due to a considerably higher Seebeck coefficient. Also in Fig. 8, one can see the sensor response to gas flows with various currents in the heater. The heater current must be low enough not to damage the PET substrate. Curves (a), (b), and (c) in this figure correspond to heater currents of 10, 15, and 20 mA, respectively. As can be seen, sensors show a moderate increase in their value at slight values of gas flow, which could be due to the direction of gas flow leading to more heat transfer from the heating part to thermocouples. At flow levels of more than 500 ccm, thermocouples present a considerable drop in their response, mainly due to the

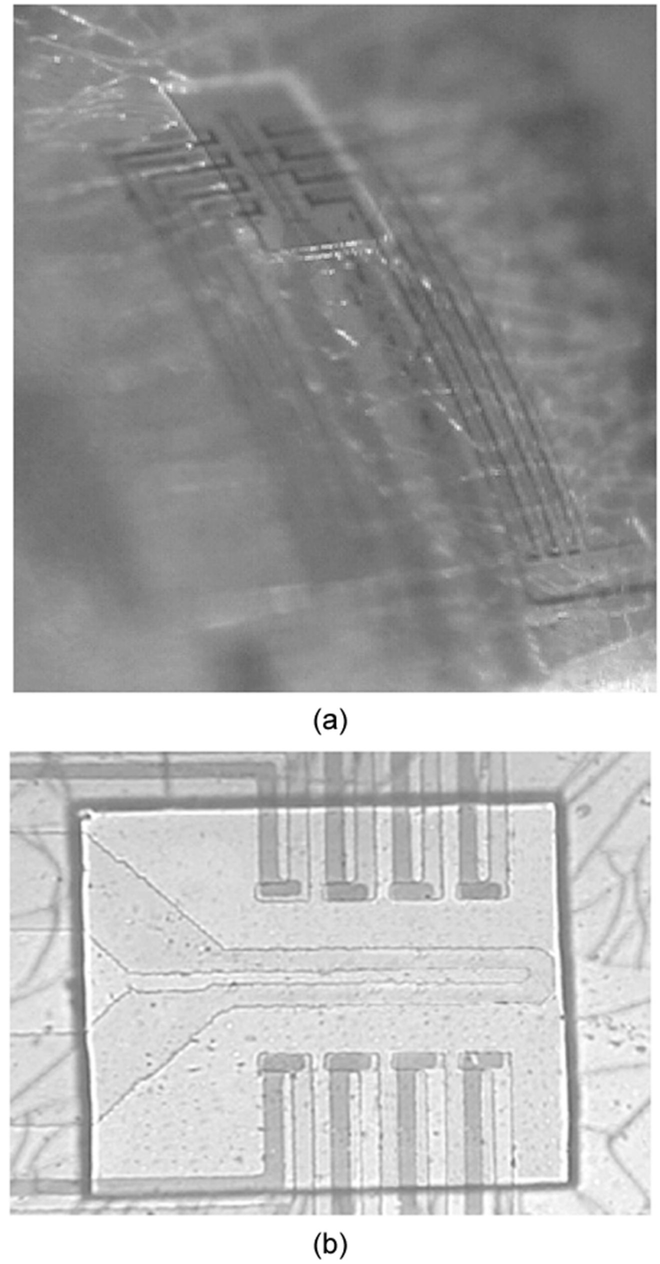


Fig. 12. (a) Completed thermo-array on a 30-μm-thick membrane. (b) Top view of the sample showing the thermo-array on the membrane. Since the PET substrate is transparent, the streaks on the back surface are visible from top side.

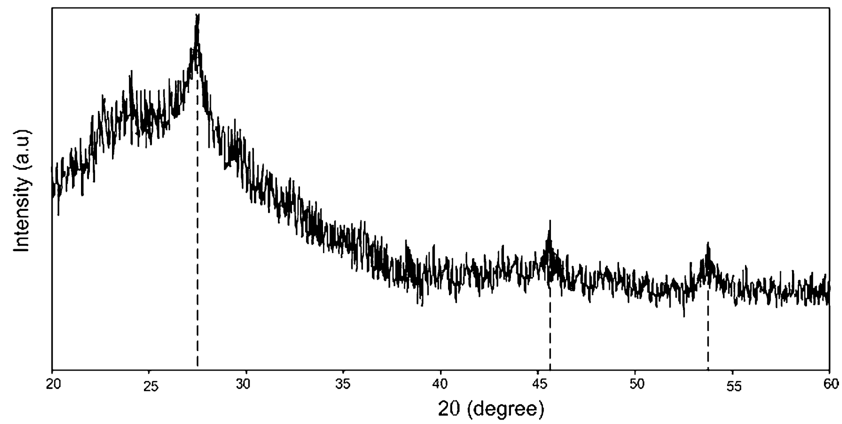


Fig. 13. XRD spectrum of partially crystallized Ge on rubber-coated glass, evidencing partial crystallization of the Ge layer.

cooling of the heater by the external basis of the temperature difference between the cold and the hot junction, which is not only a function of the thermocouple sensitivity, but also a strong function of how the generated heat in the membrane is dissipated through the substrate. This dissipation must be minimized to develop a more significant temperature difference. Although the realization of high sensitivity thermocouples is possible on PET, the overall device performance requires formation of thin membranes on plastic substrates. PET is a tough material and cannot be easily dissolved. The laser micromachining requires complex facilities and is expensive. As an alternative, we are developing a wet chemical etching process in which strong solvents, such as di-methyl-formamide (DMF) and di-chloromethane (DCM) are used in the presence of 360-nm ultraviolet illumination. Intensity of the UV source plays a crucial role in the rate that etching performs. With UV intensities less than 2 mW/cm^2, no considerable etching is observed. The schematic setup used for this study is shown in Fig. 9. The top quartz lid allows the ultraviolet light to reach the sample without losing solvent vapors. Energetic UV photons can enhance the dissolution of PET at places where opening is made in an opaque and inorganic mask. In this study, we have used a multilayer of Ge and Cu as the masking layer and the bottom side of the sample is mechanically protected. It has been observed that DCM leads to a nonuniform etching, whereas using DMF leaves smooth surfaces at the bottom of etched craters. The depth of the crater has been measured using a Dek-Tak3 stylus profilometer. The top image in Fig. 10 shows the results of depth measurement for two samples treated with DCM and DMF, respectively. The data for the sample etched with DCM shows a nonuniform etching of the crater, whereas the sample treated with DMF releases a smooth and deep crater. The bottom image in Fig. 10 yields the SEM micrograph of a membrane made using this technique and in the presence of DCM. An overall depth of 40 μm has been achieved after 7 h of etching. Streaks on the surface are a result of mask damaging during the etching process. Also, walls in this image are not sharp and well defined. By using DMF and at a temperature of 115 °C, the etching shows a superior result with less damage in the masking layer and sharp and well-defined walls are emerged. Also, the etch rate rises to an average value of 12-μm/h. Fig. 11(a) shows the SEM micrograph of the sample etched for 7 h to form an 80-μm-deep crater. Although one can see the remaining of the streaks on the surface of the PET, they are not too deep to hamper the etching process. Sharp edges at the sidewalls are better observed in Fig. 11(b). In Fig. 12(a), one can see a completed thermo-array on a 30-μm-thick membrane under bent. Fig. 12(b) gives a closer look at the device where the membrane is discernible as the large box. The Ge/Al devices are placed on one side of the PET substrate whereas the crater formation has been carried out from the opposite surface. The transparency of the substrate allows one to observe the streaks on the protected area at the back surface of the sample.

Parallel to this work, we have also fabricated poly-Ge/Al thermocouples on parlon-chlorinated rubber membranes on thin glass substrates. Spin coating of rubber-dissolved DMF is used to form a 0.5-μm-thick layer of rubber on the glass substrate. The crystallization temperature is as high as 200 °C. Fig. 13 displays the XRD spectra obtained from partially crystallized Ge on a rubber-coated glass substrate. The $\langle 111 \rangle, \langle 110 \rangle$, and $\langle 100 \rangle$ orientations of Ge are quite discernible is this figure. The hump observed in this spectrum is due to the glass substrate. The formation of rubber membranes is feasible through the backside etching of glass. The thermopiles made using this approach show superior performance, compared to their Ni-Cr metallic counterparts, and are being tested for infrared detection.

III. Conclusion

In conclusion, we have successfully realized Ge-based thermocouples on PET and rubber-coated glasses. Thermocouples made using this approach show superior performance over their metallic counterpart, mainly due to higher Seebeck factor of Ge/Al junctions. Such devices can be exploited in realizing flexible infrared imagers and detectors, provided that the addressing transistors can be integrated on PET, as well. In addition, we have introduced a new micromachining technique in which the energetic UV photons promote etching of PET in the direction of UV exposure. This technique can be used in making thin membranes on PET substrates. We are also working on the crystallization of Ge/Si alloys for the possible fabrication of high-performance Si/Ge thermocouples on flexible substrates. The use of such devices to make infrared detectors is underway.

REFERENCES

[1] A. V. Wagner, R. J. Foreman, L. J. Summers, T. W. Barbee, and J. C. Farmer, "Fabrication and testing of thermoelectric thin film devices," in *Proc. Int. Conf. Thermoelectrics*, Mar. 1996, pp. 269–273.

[2] M. C. Foote, E. W. Jones, and T. Caillat, "Uncooled thermopile infrared detector linear arrays with detectivity greater than 10^9 cmHz$^{1/2}$/W," *IEEE Trans. Electron Devices*, vol. 45, pp. 1896–1902, Sept. 1998.

[3] M. Muller, W. Budde, R. Gottfried, A. Hubel, R. Jahne, and H. Kuck, "A thermoelectric infrared radiation sensors with monolithically integrated amplifier stage and temperature sensor," *Sens. Actuators A*, vol. 54, pp. 601–605, June 1996.

[4] A. W. Van Herwaarden, D. C. van Duyn, and J. Groeneweg, "Small-size vacuum sensors based on silicon thermopiles," *Sens. Actuators A*, vol. 27, pp. 577–581, May 1991.

[5] A. Glaninger, A. Jachimowicz, F. Kohl, R. Chabicovsky, and G. Urban, "Wide range semiconductor flow sensors," *Sens. Actuators A*, vol. 85, pp. 139–146, Aug. 2000.

[6] P. Kopystynski, E. Obermeier, H. Delfs, W. Hohenster, and A. Loser, "Silicon RF power sensor from DC to microwave," in *Proc. Int. Conf. Micro. Electro., Opt., Mech. Syst. Comp.*, 1990, p. 605.

[7] E. Schreck, R. E. Fontana, and G. P. Singh, "Thin film thermocouple sensors for measurement of contact temperatures during slider asperity interaction on magnetic recording disks," *IEEE Trans. Magn.*, vol. 28, pp. 2548–2550, Sept. 1992.

[8] E. Fortunato, I. Ferreira, F. Giuliani, and R. Martins, "Large area flexible thin film position sensitive detectors," *Sens. Actuators A*, vol. 86, pp. 182–186, Nov. 2000.

[9] P. Van Gerwen, T. Slater, J. B. Chevrier, K. Beart, and R. Mertens, "Thin-film boron-doped polycrystalline silicon$_{70\%}$-germanium$_{30\%}$ for thermopoles," *Sens. Actuators A*, vol. 53, pp. 325–329, May 1996.

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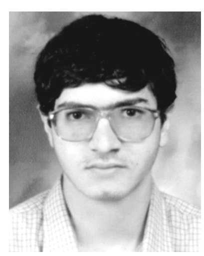

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