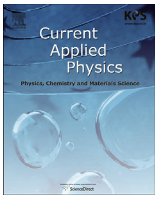
Current Applied Physics 16 (2016) 1511–1516

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap



Local crystallization and enhanced thermoelectric performance of glassy carbon induced by the electron beam irradiation

Inseon Oh [a], Junhyeon Jo [a], Jungmin Park [a], Jongmin Lee [b], Heungjoo Shin [b], Jung-Woo Yoo [a, *]

[a] *School of Materials Science and Engineering, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea*

[b] *Department of Mechanical Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea*

ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form
16 August 2016
Accepted 27 August 2016
Available online 29 August 2016

Keywords:
Glassy carbon
Raman spectroscopy
Seebeck coefficient
Thermoelectricity
Electron-beam irradiation

ABSTRACT

Glassy carbon can be used in a variety of harsh environments because it exhibits low electrical resistance, high thermal stability, chemically impermeability and hardness. In this work, we studied the potential application of the pyrolized glassy carbon as a thermoelectric material by electron beam irradiation. Irradiation with electron beam energy of 1.4 MeV and 0.2 MeV triggered local crystallization of glassy carbon, which was determined by a Raman spectroscopy. As the irradiation time was increased, the number of sp^2 hybridized carbons was gradually increased while the number of disordered carbons was decreased. This electron beam induced local crystallization caused a synergetic effect on a thermoelectric power factor of the studied glassy carbon films. Although the electrical conductivity was decreased by the e-beam irradiation, the Seebeck coefficient was significantly enhanced resulting in an improved power factor. The optimal power factor we obtained for the irradiated glassy carbon was ~50% higher than that of the non-irradiated sample.

1. Introduction

Thermoelectricity, which can generate electric energy from waste heat and provide cooling or heating for an enclosed space, is a promising candidate for the future renewable energy source. In general, thermoelectric devices are silent, scalable, and simple to be ubiquitous applications, because they are solid state with no moving parts. Optimization of the performance of thermoelectric materials involves with complex tuning of materials properties as their performance efficiencies are determined by a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$; where S, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Thus, the desired properties for an ideal thermoelectric material are large Seebeck coefficient, high electrical conductivity, and low thermal conductivity, referring as a “phonon glass, electron crystal (PGEC)” [1]. Unfortunately, these properties are not independent and entangled each other through trade-off relations. For instances, materials having high electrical conductivity generally have low Seebeck coefficient. The thermal conductivity largely relies on the phonon transport, but contribution from free electrons becomes more considerable as the electrical conductivity get stronger. Thus, fine-tuning of material properties toward efficient thermoelectricity is extremely challenging.

Traditionally, thermoelectric materials, such as Bi, Te, Se, and Pb, and their alloys have been most widely used for various thermoelectric home appliances [2,3]. A number of complex structures of these materials, such as complex crystals, nano-composites, and thin film superlattices, have been developed to reduce lattice thermal conductivity. Such nano-material engineering has recently brought a significant improvement in the thermoelectric efficiency [4–7]. However, these inorganic materials have drawbacks of rareness, expensive cost, and high temperature for the optimal operation.

Recently, studies of thermoelectric properties of carbon-based materials such as conducting polymers and other carbon allotropies have been under intense research because organic materials could be cheap, flexible, abundant, easy to synthesis, and suitable for large area fabrication. The intrinsically lower thermal conductivity than inorganic thermoelectric materials is an additional merit

---

* Corresponding author.
E-mail address: jwyoo@unist.ac.kr (J.-W. Yoo).

http://dx.doi.org/10.1016/j.cap.2016.08.017
1567-1739/© 2016 Elsevier B.V. All rights reserved.

regarding thermoelectric efficiency. As one of the most widely used conducting polymers, a poly(3,4-ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) could have enhanced thermoelectric performance with improved electrical conductivity and Seebeck coefficient by the secondary doping process [8,9]. The highest *ZT* value of ~0.42 at room temperature was achieved by optimizing carrier concentration and morphology of the PEDOT:PSS [8,9].

For other examples, it was found that the power factor of the carbon-based composite can be greater than that of individual material, by complementing pro and con of each material [10,11]. The nano-material-based composites, such as carbon nanotube(CNT)/polymers exhibited enhanced thermoelectric performance by controlling electron transport network. The single-walled(SW)-CNT/poaniline(PANI) nano-composites showed enhanced *ZT* value of 0.004 attributed to the enhanced mobility through the ordered chain structures of the PANI [12]. CNT-polymer composite showed that electrical conductivity can be dramatically increased by creating a network of CNTs in a composite [13]. A non-covalently functionalized graphene mixed with a semiconducting fullerene demonstrated the *ZT* value as high as 0.067, when the ratio of the fullerene to the graphene was 3:7 [14]. However, these approaches for developing thermoelectric materials require synthesis of nanomaterials, which limits the mass production for wide applications. Accordingly, we aim to introduce a new paradigm of top-down and large scale material production to realize the mass production with low price by the electron (e)-beam irradiation on glassy carbon thin films. Glassy carbon (GC, vitreous carbon) is a non-graphitizing carbon which combines glassy and ceramic properties with those of graphite. GC has good electrical conductivity and low thermal conductivity caused by an amorphous structure. It has been used for various structural materials with low electrical resistance, impermeability to gas and liquids, hardness, and low density [15]. Many of these merits of GC can be exploited for a variety of thermoelectric applications. E-beam irradiation is an effective method for the structural transformation by inducing cross-linking, radical, and scissoring reactions [16,17] so that it could control dopants in GC.

In this work, we explored a new approach for the development of carbon-based nano-structured thermoelectric materials by using e-beam irradiation. The e-beam irradiation induces a local crystallization of GC, which leads to reduced disordered carbons and increased sp^2 hybridized carbons. This electron beam induced doping in GC leads to a synergetic effect on a thermoelectric power factor. In particular, the optimal power factor ($P = S^2\sigma$) of irradiated GC film was 50% higher than that of non-irradiated sample. This study introduces a new top-down approach for developing carbon-based nano-material composites, which could be a promising methodology for an alternative thermoelectric energy harvesting.

2. Experimental details

The schematic fabrication steps of GC thin films are described in Fig. 1. First, a quartz substrate (7 mm × 15 mm) was cleaned with acetone, ethanol, and de-ionized water in ultrasonic cleaner bath for 20 min in sequence and dried by using N$_2$ gas. A negative photoresist (SU-8 2010, MicroChem, Corp., Newton, MA, USA) was spin-coated onto the quartz substrate, followed by a soft baking at 95 °C for 7 min. Typical thickness of spin-coated resist was ~10 μm. A UV exposure (150 mJ/cm^2) was done through a photo mask pattern of a rectangle (3 mm × 11 mm). The UV exposed films were then baked at 95 °C for 2 min before the development step. The patterned SU-8 films were pyrolyzed in a vacuum furnace so that the films were converted into monolithic carbon structures. The pyrolysis process consisted of a pre-baking step for major volume reduction and a carbonization step for forming a solid carbon. During pre-baking, the thin films were heated to 350 °C at a rate of 1 °C/min and maintained at that temperature for 60 min. The temperature was then increased to 900 °C at a rate of 1 °C/min and maintain at that temperature for 60 min. Finally, the films were steadily cooled down to the room temperature.

The electron-beam (e-beam) irradiation was performed by e-beam accelerator equipped in Korea Atomic Energy Research Institute (KAERI, Korea) with controlled beam energy and beam current. For our experiments, the low-energy (0.2 MeV) and high-energy (1.4 MeV) e-beam irradiations on GC thin films were

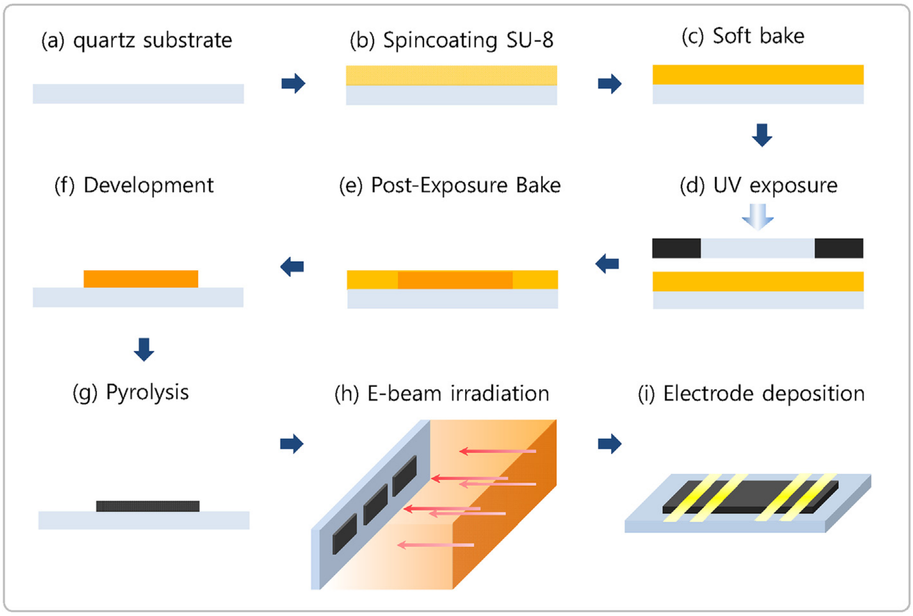


Fig. 1. Schematic steps of the preparations of GC thin films and e-beam irradiation. (a) A quartz substrate, (b) spin-coating SU-8, (c) SU-8 soft baking, (d) UV exposure for pattern, (e) post-exposure baking, (f) development, (g) pyrolysis process, (h) e-beam irradiation on GC thin films (i) electrode deposition.