A fundamental study of phase separation in GaAs-Ge system for semiconductor fibers by post heat treatments

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Abstract

Fiber optics serve many uses in our society today, they are used to send internet, tv, telephone, and other computing signals around the world. They also have uses in the field of surgery and dentistry, as well as, military applications[1,3,9]. Replacing the normally silica core with a core of semiconducting material would allow us to send different wavelengths of light and possibly change the optical properties of the fiber itself. Previous research has been done for the use of germanium as a semiconducting core material[6]. In this paper we analyze the effects of heat treatment on the phase separation of a GaAs-Ge system with the intent to later use the resulting phase separation method to produce a SiGa core fiber. We observe the effects of differing treatment times on the separation.

Introduction

Original research regarding semiconductor core optical fibers used silica as the core material for the fiber[4,7]. However, recently other semiconductor materials with a higher infrared transparency have become of interest since they would be good candidates for infrared transmission fibers[6].

The main obstacles that have been faced when trying to produce these fibers is that when the fibers are produced in traditional fiber-tower draw processes, the infrared transparency of the fibers has been low which has led to high attenuations[8]. Research has also been performed looking at the use of CO_2 laser irradiation to produce SiGe-core optical fibers[2]. For this process, germanium is mixed with silicon and the SiGe is then drawn into the core of the fiber. Once the fiber is cooled, we are then able to use laser heating to create germanium rich sections within the fiber.

Our purpose for this research is to use GaAs and Ge in the laser heating fabrication method. Our goal is to use this separation to create GaAs core fibers that can be used for infrared transmission with lower attenuation than previously produced fibers. We need to draw the fibers as a GaAs-Ge core because by combining these two elements we lower the melting point as compared to using only GaAs in the core. This is useful because the melting point of GaAs is too high for it to be used in traditional fiber drawing techniques[10].

Experimental

To begin, a batch of Ge-GaAs was made by mixing 2.75 grams (16 mole percent) of GaAs and 7.25 grams (84 mole percent) Ge. This ratio was chosen because it made the melting point of the mixture close to $1000^{o}c$[10] which is what was needed for the fiber drawing process. The mixture was then evenly distributed between three silica glass crucibles. The crucibles were then sealed on the lathe with vacuum being pulled. The samples were then melted in the furnace

at 950ºc for 8 hours. After melting, the samples were cooled and removed from the crucible. Next, another set of silica glass tubes were drawn using the Heathway fiber draw tower at Clemson University. Four samples of the melted Ge-GaAs were placed into the new glass crucibles and again vacuum was drawn on the crucibles and they were sealed. Large fibers (canes) were drawn at the Heathway draw tower using the molten core method[5]. The preform was made using Ge-GaAs and DURAN® borosilicate glass cladding tube (Schott North America Inc., Elmsford, NY, USA) with a composition of $81SiO_{2–13B2O3–4Na2O–2Al2O3}$ (in wt%) . The cane was drawn at 990ºc with an outer diameter of 3.5mm and a core diameter of 350um. The cane was then cleaved into 5 small samples for heat treatment. All samples were heat treated at 850ºc with treatment times of 12, 36, and 72 hours.

A. X-ray diffraction

Powder x-ray diffraction was done using a Rigaku MiniFlex X-ray Diffractometer. Diffraction patterns were collected from 5^O to 70^O in 2-theta in 0.02^O steps. Samples were analyzed as fine powders. Three powder samples were made for XRD, one of germanium, one of gallium arsenide and another with the melted Ge-GaAs sample.

B. Microscopic and Elemental Analysis

All samples observed were set in an epoxy mold and were then mechanically polished using silicon carbide (SiO) bonded paper ranging from 800 to 1200 grit. SEM was performed using a Hitachi SU5000 variable pressure field emission scanning electron microscope running at 20kV and a 10mm working distance. EDX was performed to analyze the distribution of elements in the samples.

Results and Discussion

Image 1 and its corresponding table 1 are used to confirm that we had proper melting and combining of the Ge and GaAs. This also allows us to see that there was little oxidation (approx. 2 atomic % of oxygen) of the samples.

Image 2 and table 2 show that after 12 hours of heat treatment we see no evidence that the system has undergone any phase separation since the distribution of elements was similar to that of the non-treated sample.

Image 3 and graph 1 show the compositional changes across the transverse of the fiber. There are signs that there may be some separation happening because as we scan across the cane we see the gallium and arsenic peak up at the edges of the core. This leads us to think that the GaAs might be separating away from the core and leaving germanium rich areas in the center. This is further supported by the fact that the gallium and arsenic both peak and fall at similar points and in similar atomic percentages.

Image 4 and graph 2 still shows the similar peak formations of the Ga and As at the edges but the peaks have kept relatively the same height which is not what we expected to see if this was movement of GaAs to the edges of the cane. When we performed mappings on the 72 hours sample, as seen in Image 5 and 6, we see bright pink spots forming randomly in the cane. This indicates areas of high gallium concentration which is a good indicator of phase separation. Tables 3 and 4 show point scans of the gallium rich areas compared to areas where we see a more baseline composition. What we see is in these gallium rich areas we see arsenic also peak which shows that Ga and As are forming together in these areas.

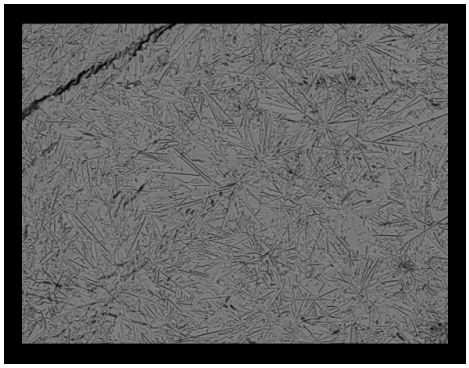
Conclusions and Further Research

We see some evidence for phase separation of GaAs and Ge after longer (36+ hours) heat treatment. At 36 and 72 hours of treatment we see what could be transverse separation of gallium and arsenic. The transverse separation could have been caused when the system was heated to draw the cane. The strongest evidence for separation occurs after 72 hours of heat treatment because we begin to see gallium and arsenic forming cluster throughout the core of the cane.

For continued research, we plan to send the samples to the Norweigen University of Science and Technology to be treated using their CO_2 laser heating method. This treatment should allow for more controlled separation of the GaAs. If we see successful separation of the GaAs we could then move on to applying this process to a SiGa system to test its optical properties. We also

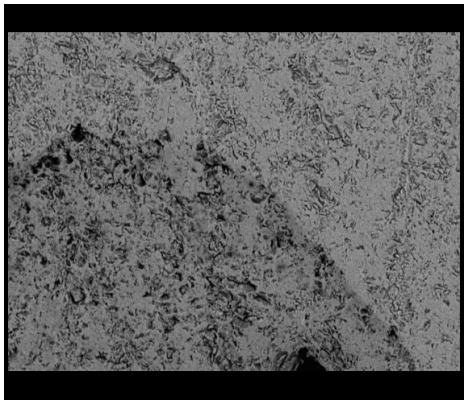
have the possibility to treat the samples for longer than 72 hours to see if more phase separated clusters occur.

Figures



		Atomic	%	
Spectrum Label	O	Ga	Ge	As
Map Sum Spectra	2.04	12.19	75.24	10.53

Image 1 shows SEM of the non-treated sample. Table 1 shows the elemental composition found using EDX



		Atomic	%		
Spectrum Label	O	Ga	Ge	As	C
Map Sum Spectra	2	9.8	59.7	8.2	18.8

Image 2 shows SEM of the 12 hour treated sample and Table 2 show the corresponding EDX results

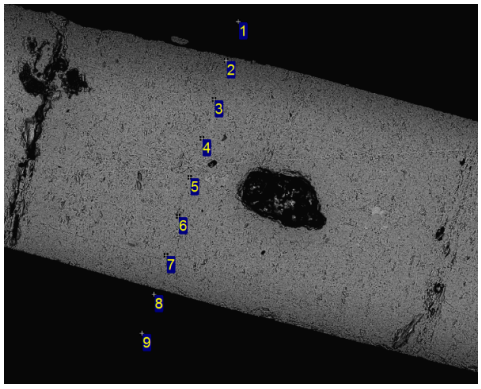
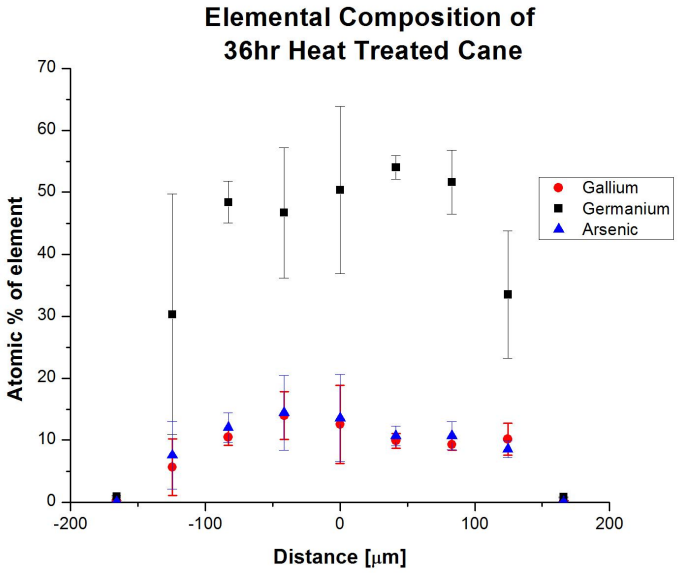


Image 3 shows SEM of the 36 hour treated sample



Graph 1 shows the combined results of the line scans of the 36 hour sample

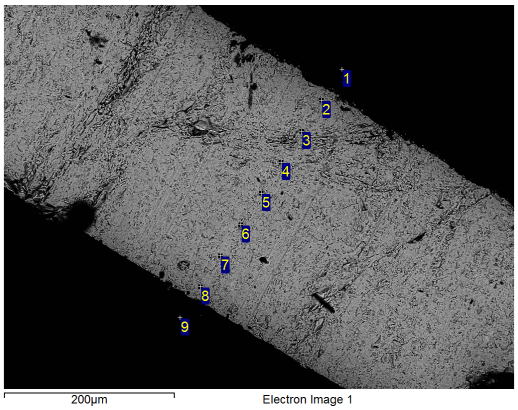
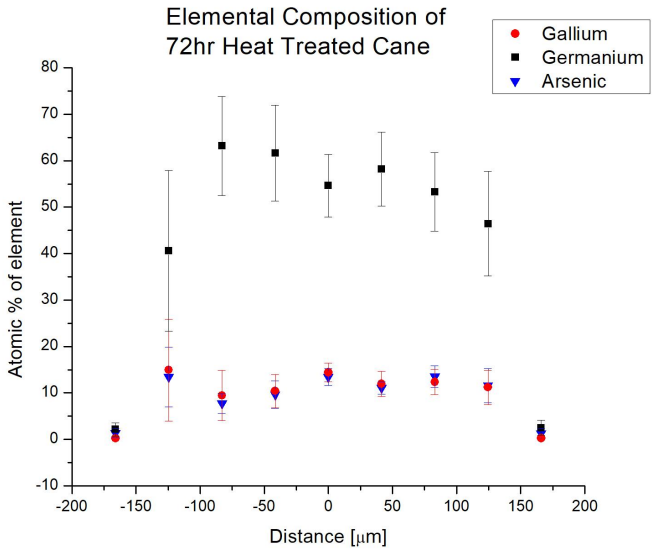


Image 4 shows SEM of the 72 hour treated sample



Graph 2 shows the combined results of the line scans of the 72 hour sample

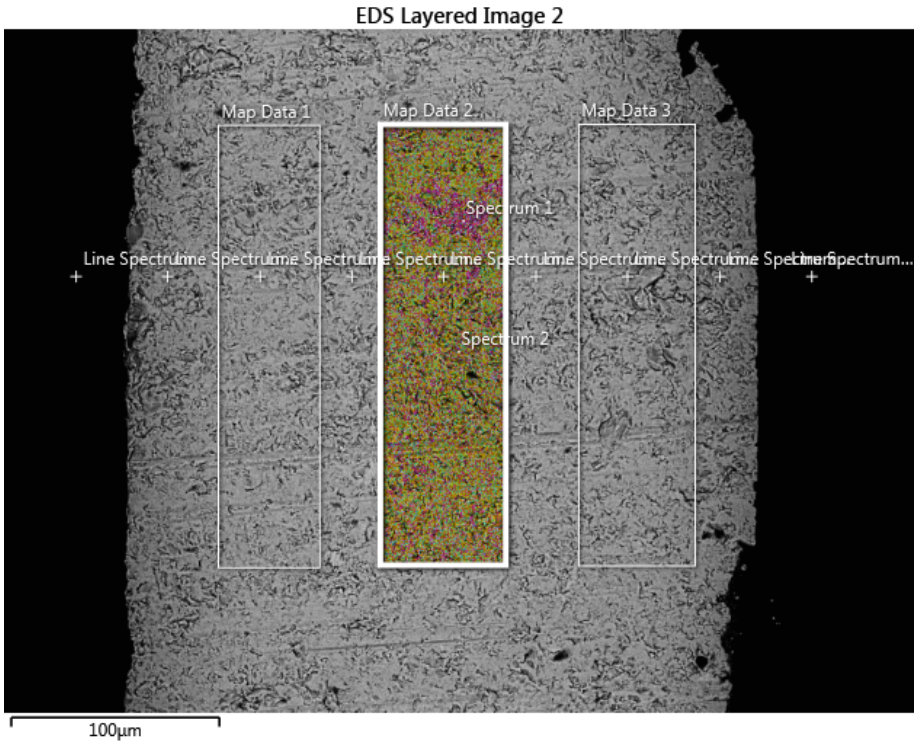


Image 5 shows EDX mapping of the 72 hour sample (Ga is shown in pink)

Element	Spectrum 1 (Atomic %)	Spectrum 2 (Atomic %)
Ga	33.9	9.4
As	31.8	9.7
O	15.4	15.7
Ge	11.6	58.1
Si	7.4	7.2

Table 3 shows the results of a point scan of the Ga rich area (spectrum 1) and a baseline area (spectrum 2)

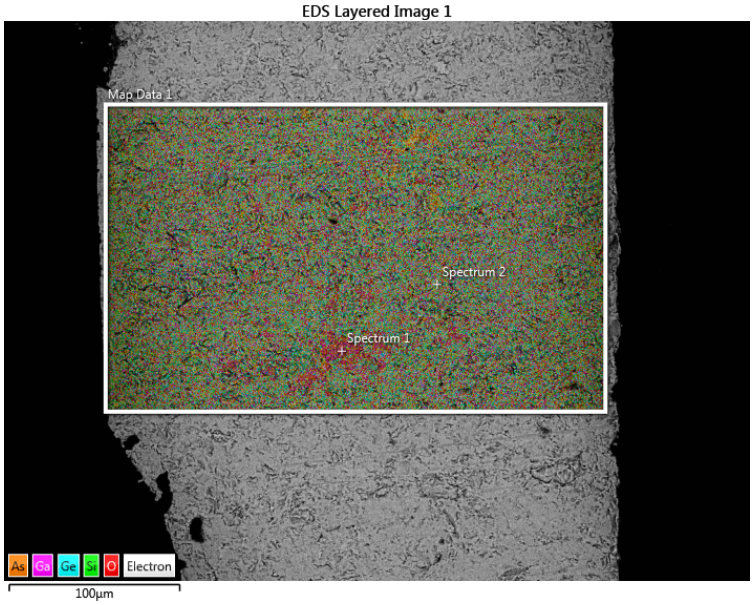


Image 6 shows EDX mapping of the 72 hour sample

Spectrum Label	C	O	Si	Ga	Ge	As
Spectrum 1	33.35	9.94	4.56	23.97	8.40	19.77
Spectrum 2	35.27	10.04	4.54	5.60	40.20	4.35

Table 4 shows the results of a point scan of the Ga rich area (spectrum 1) and a baseline area (spectrum 2)

References:

[1]B. Jackson, P. Sazio, and J. Badding, “Single crystal semiconductor wires integrated into microstructured optical fibers,” Adv. Mater. 20(6), 1135–1140 (2008).

[2]David A. Coucheron, Michael Fokine, Nilesh Patil, Dag Werner Breiby, Ole Tore Buset, Noel Healy, Anna C. Peacock, Thomas Hawkins, Max Jones, John Ballato, Ursula J. Gibson, “Laser recrystallization and inscription of compositional microstructures in crystalline SiGe-core fibres,” Nature Communications, 13265 (2016)

[3]D.-J. Won, M. Ramirez, H. Kang, V. Gopalan, N. Baril, J. Calkins, J. Badding, and P. Sazio, "All-optical modulation of laser light in amorphous silicon-filled microstructured optical fibers," Appl. Phys. Lett. 91(16), 161112 (2007).

[4]J. Ballato, T. Hawkins, P. Foy, R. Stolen, B. Kokuoz, M. Ellison, C. McMillen, J. Reppert, A. M. Rao, M. Daw, S. Sharma, R. Shori, O. Stafsudd, R. R. Rice, and D. R. Powers, "Silicon optical fiber," Opt. Express 16(23), 18675–18683 (2008).

[5]J. Ballato, T. Hawkins, P. Foy, B. Kokuoz, R. Stolen, C. McMillen, M. Daw, Z. Su, T. Tritt, M. Dubinskii, J. Zhang, T. Sanamyan, and M. J. Matthewson, "On the Fabrication of All-Glass Optical Fibers from Crystals," J. Appl. Phys. 105(5), 053110 (2009).

[6]J. Ballato, T. Hawkins, P. Foy, B. Yazgan-Kokuoz, R. Stolen, C. McMillen, N. K. Hon, B. Jalali, and R. Rice, "Glass-clad single-crystal germanium optical fiber," Opt. Express 17, 8029-8035 (2009).

[7]J. Ballato, T. Hawkins, P. Foy, B. Yazgan-Kokuoz, C. McMillen, L. Burka, S. Morris, R. Stolen, R. Rice, "Advancements in semiconductor core optical fiber," Progress in Materials Science, Volume 16, Issue 6, 2010

[8]J. Ballato, T. Hawkins, P. Foy, S. Morris, N. K. Hon, B. Jalali, and R. Rice, "Silica-clad crystalline germanium core optical fibers," Opt. Lett. 36, 687-688 (2011)

[9]P. J. Sazio, A. Amezcua-Correa, C. E. Finlayson, J. R. Hayes, T. J. Scheidemantel, N. F. Baril, B. R. Jackson, D. J. Won, F. Zhang, E. R. Margine, V. Gopalan, V. H. Crespi, and J. V. Badding, "Microstructured optical fibers as high-pressure microfluidic reactors," Science 311(5767), 1583–1586 (2006).

[10]Y. Taskeda, T. Hirai, M. Hirao (1964). Phase Diagram for the Pseudo-Binary System Germanium and Gallium Arsenide. *Journal of Electrochemical Society, 112 3*, 364