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RESEARCH ARTICLE

Growth of SrGaGe Nanowires by Thermal Annealing

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ABSTRACT

SrGaGe is a type-I clathrate and displays glass-like thermal conductivities along with good charge carrier mobility, which makes it an interesting material for thermoelectric research. SrGaGe one dimensional nanostructures gained considerable interest due to even lower thermal conductivity. In nanowires, the lattice contribution to thermal conductivity approaches the amorphous limit for buck materials. In this paper, we report a simple fabrication technique for making large quantities of SrGaGe wires with diameters ranging from 30 nm to 80 nm. The nanowires showed strong preferential growth with gold catalyst presented. Presented here are the growth conditions and images of the resulting wires that were fabricated. The products are characterized by Scanning Electron Microscopy (SEM).

Keywords: Nanowires, Thermoelectric materials, Thermal annealing, SEM, VLSI, Growth mechanism.

1. INTRODUCTION

The vapour-liquid-solid growth mechanism was reported by Wagner and Ellis in 1964 [1]. In their report, a chemical vapour deposition technique was used to fabricate high aspect ratio silicon wires with diameters of 200µm. Many reports have followed this initial work [2, 3, 4], with more recent efforts focused on diameter in the submicron and nanoscale ranges with reported diameters down to 3nm [5, 6]. Both chemical vapour deposition (CVD) and physical vapour deposition (PVD) techniques have been utilized in the fabrication of nanowires through the vapor-liquid-solid technique [7, 8, 9, 10]. More recently, an Oxide Assisted (OA) technique has been proposed as another mechanism for the growth of nanowires [11]. In this study a PVD method was used to grow the SrGaGe nanowires. Physical vapour deposition (PVD) involves atoms and/or molecules of a material that are deposited from the gas(or vapour) phase onto a substrate without a chemical reaction step taking place. Various mechanisms can be used to get the material into the gas phase including, thermal evaporation, sputtering, pulsed laser deposition, cathodic arc and molecular beam epitaxy.

During the PVD process, material from a liquid or solid source is transported through the gas phase to a substrate. In placing the atoms or molecules from the source into the vapor phase, the particles are raised in energy. As the particles arrive, their energy is taken away by a cooler substrate surface facing the source which allows the particles to form a solid thin layer. The atoms or molecules in the vapour phase will condense on the substrate after some surface diffusion of the adatoms. Accommodation of the adatoms occurs as the Gibbs free energy ΔG, is sufficiently reduced during condensation. Since ΔG is further reduced for adatoms that form clusters or accommodate to step edges, there is a preferential growth of films along such defects and/or in island formations.

Assuming the incident kinetic energy is not too high, an atom striking a surface will lose its velocity component normal to the surface in a short time. The incident vapour atom is then physically adsorbed and called an adatom. It may or may not be completely thermally equilibrated with the surface. If not equilibrated, it can move over the surface by jumping from one potential well to another as driven by thermal activation from the surface

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and/or by its own kinetic energy parallel to the surface. The adatom has a finite stay or residence time on the surface during which it may interact with other adatoms to form a stable cluster and be chemically adsorbed (incorporated into the surface) with the release of the heat of condensation. If not adsorbed, the adatom re-evaporates (desorbs) into the vapour phase. Therefore, condensation is the net result of an equilibrium between the adsorption and desorption processes.

2. SrGaGe

Thermoelectric materials could be used to convert temperature gradients to electricity. Thermoelectric materials are measured by the dimensionless parameter ZT- a function of absolute temperature, electrical conductivity, thermal conductivity and Seebeck coefficient. To have a high ZT thermoelectric material, thermal conductivity needs to be as low as possible. For nanowires, the lattice contribution to thermal conductivity approaches the amorphous limit for buck materials [12-17]. SrGaGe is a type-I clathrate and displays glass-like thermal conductivities along with good charge carrier mobility, which makes it an interesting material for thermoelectric research [18-20]. We produced nanowires from SrGaGe simply by mixing it with Au nanoparticles and annealing. To our knowledge, this material has not previously been grown in the form of nanowires. Hence, the successful growth of clathrate nanowires would establish the foundation for further studies of this thermoelectric material.

3. EXPERIMENTS

SrGaGe powder was mixed with gold nanoparticles and annealed at 800 C for 120 minutes. In the VLS growth mechanism, a metal catalyst is required. Gold nanoparticle was used as the metal catalyst [21]. In our experiment the SrGaGe pile was mixed with colloidal Au of 20nm nominal size with polylisine-L to avoid colloidal clustering. The sample was placed on top of a quartz plate and subsequently annealed to 800 C for 120 minutes. The experiment was conducted within a quartz tube (outer diameter, 90mm; length, 80cm) heated by a horizontal tube furnace. The sample was put on a quartz boat and placed at the center of the quartz tube that was evacuated to about 30 mTorr. A background gas of argon was used at a flow rate of 200sccm and this flow was maintained throughout the whole reaction. The pressure inside the tube increased from 30mTorr to 150 mTorr after the argon gas entered into the tube. The vacuum pump was used throughout the experiments.

4. RESULTS

The SEM image in figure A1 shows that the nanowires were scattered on the surface of the SrGaGe powder. There were some smaller micrometer-sized SrGaGe chunks attached to the bigger piece. This could be due to the condensation of the SrGaGe vapour. It is the same vapour which grew the SrGaGe nanowires. The dark area on the left side is the quartz plate. Nanowires with a diameter of 50nm grew on the SrGaGe powder surface and are mixed with some whiskers of bigger size. The nanowires were found to grow in selected regions and were not notably straight. Some nanowires were observed on the quartz plate close to the SrGaGe powder.

In the SEM image in figure A2, the dark region is the quartz plate. The bright area in the bottom left of the image is the SrGaGe powder. We found that most of the nanowires distributed on the bottom half of the image were close to the SrGaGe powder region. Nanowires close to the SrGaGe powder particles were found in higher densities with lengths of approximately 5μm and average diameters of 30nm, farther away from the powder particles. The density and length of the nanowires gradually decrease to negligible quantities at distances of 11μm from the powder particles. From the image, it might suggest that the solid SrGaGe first transforms into vapour form. The vapour pressure was higher and close to the SrGaGe powder. The growth of nanowires took place while the SrGaGe vapour pressure was higher.

The SEM image in figure A3 shows that nanowires were mostly scattered on the top surface of the SrGaGe powder. A mixture of larger diameter and smaller diameter nanowires can be seen by comparing the centre of the image to the nanowires at the perimeter of the powder particle. The dark area on the right side is the quartz plate. The average length of the nanowires was 4 m and the average diameter was 70nm. The scale bar is 5 m.

The histogram in figure A4 shows the diameter distributions of the SrGaGe nanowires with diameters ranging from 30nm to 80nm. The average dimension was about 52nm in

diameter. EDS was used to analyze the samples. Three major peaks, Sr, Ga and Ge were shown in the EDS. The EDS analysis in figure A5 shows the composition of SrGaGe.

5. CONCLUSION

In this experiment we have produced nanowires from SrGaGe by simply mixing it with Au nanoparticles and using a local vapour confinement technique. The gold balls clearly appeared at the tips, which indicate that the growth mechanism is a well-known vapour-liquid-solid mechanism where gold particle was used as a metal catalyst. Thermal treatment of SrGaGe powder at 800^0C under Ar flow lead to the growth of nanowires with diameters ranging from 30 to 80 nm. Nanowires only grew when gold particles were presented and this provided information about the VLS growth mechanism in the SrGaGe-gold system. We have presented a simple fabrication technique for making large quantities of SrGaGe wires with diameters ranging from 30nm to 80nm. These results open a cost-effective way to prepare low-dimensional thermoelectric materials.

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APPENDIX A

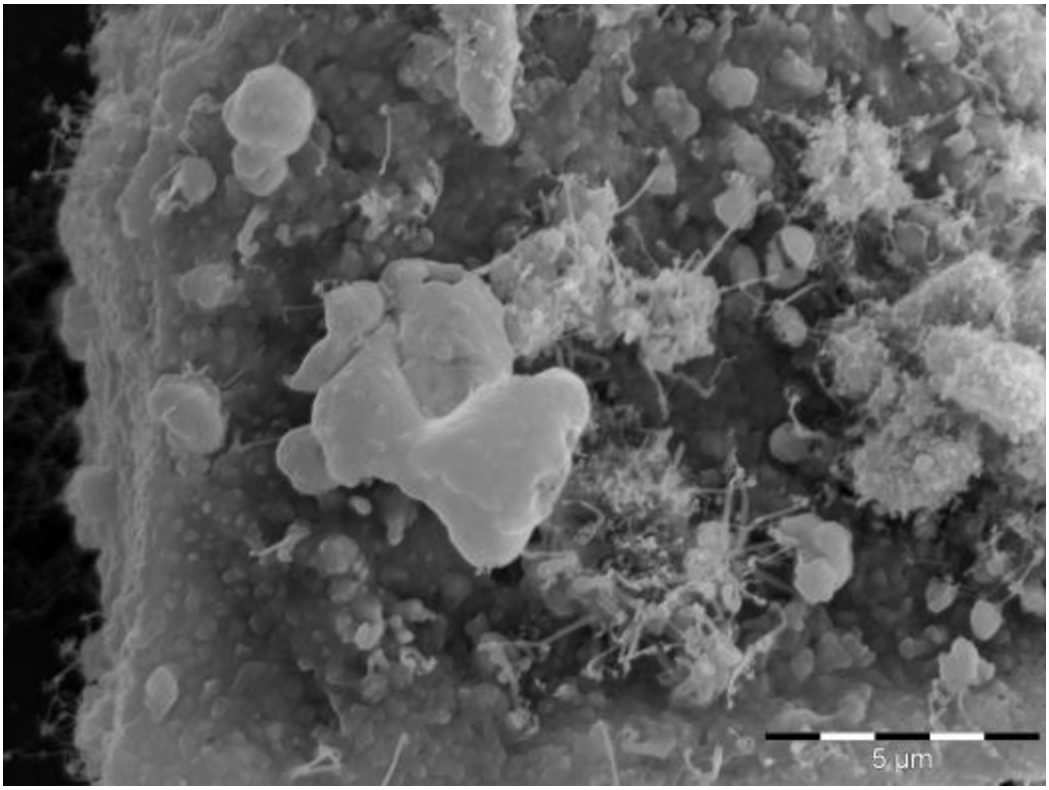

Figure A1.The SEM image shows that nanowires were scattered on the surface of $Sr_8Ga_{16}Ge_{30}$ powders. The scale bar is 5 µm.

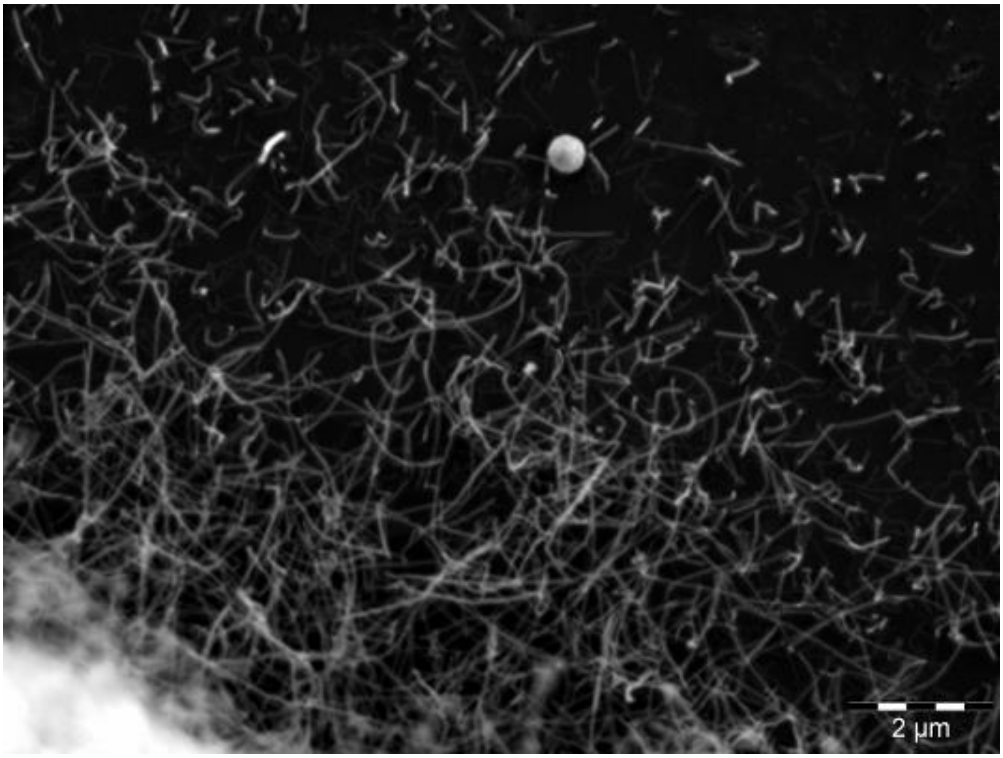

Figure A2.The SEM image shows that the dark region is a quartz plate. The scale bar is 2 µm.

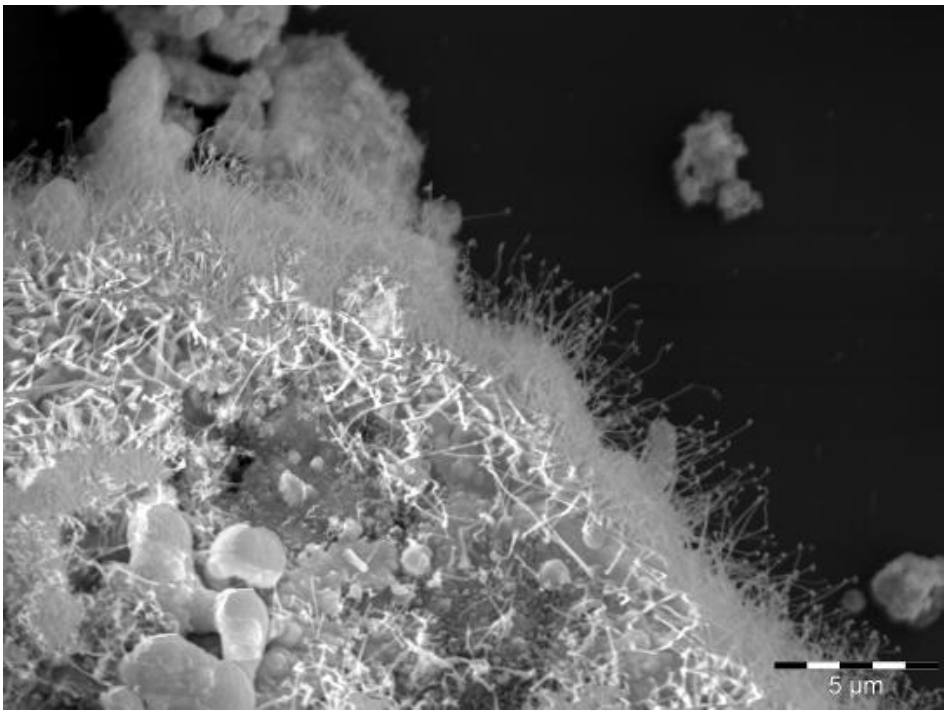

Figure A3.The SEM image shows that nanowires were mostly scattered on the top surface of the SrGaGe powder. The scale bar is 5 µm.

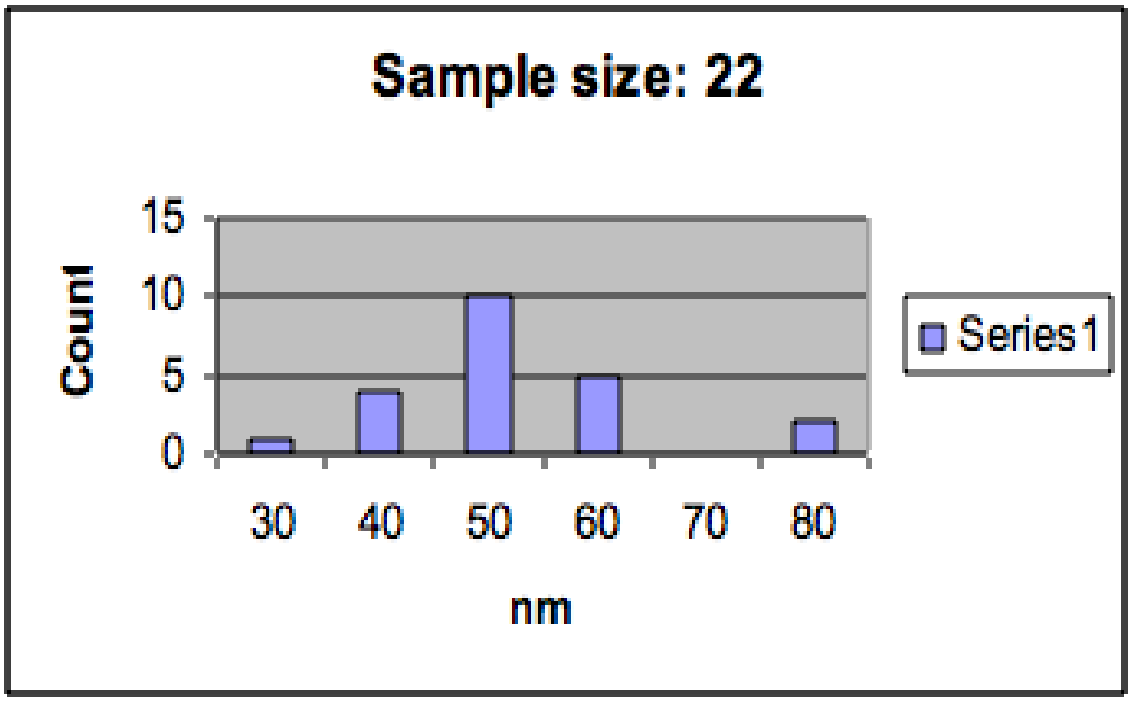

Figure A4.Histogram showing the diameter of nanowires. Total sample size: 22. Average diameter is 52 nm.

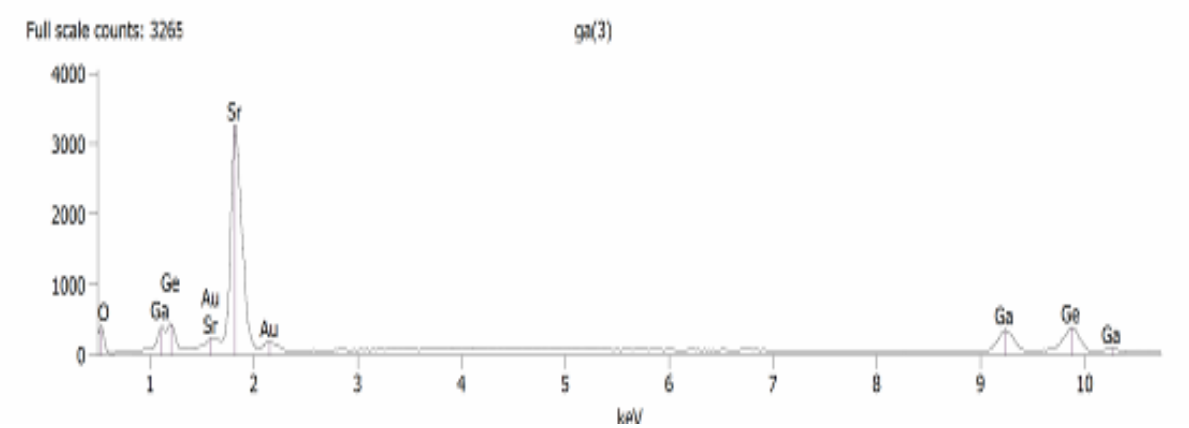

Figure A5.EDS analysis on the nanowires that grew on SrGaGe