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ARSENIC SULFIDE NANOWIRE FORMATION ON FUSED QUARTZ SURFACES

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ABSTRACT

Arsenic sulfide (As_xS_y) nanowires were synthesized by an evaporation-condensation process in evacuated fused quartz ampoules. During the deposition process, a thin, colored film of As_xS_y was deposited along the upper, cooler portion of the ampoule. The ampoule was sectioned and the deposited film analyzed using scanning electron microscopy (SEM) to characterize and semi-quantitatively evaluate the microstructural features of the deposited film. A variety of microstructures were observed that ranged from a continuous thin film (warmer portion of the ampoule), to isolated micron- and nano-scale droplets (in the intermediate portion), as well as nanowires (colder portion of the ampoule). Experiments were conducted to evaluate the effects of ampoule cleaning methods (e.g. modify surface chemistry) and quantity of source material on nanowire formation. The evolution of these microstructures in the thin film was determined to be a function of initial pressure, substrate temperature, substrate surface treatment, and initial volume of As_2S_3 glass. In a set of two experiments where the initial pressure, substrate thermal gradient, and surface treatment were the same, the initial quantity of As_2S_3 glass per internal ampoule volume was doubled from one test to the other. The results showed that As_xS_y nanowires were only formed in the test with the greater initial quantity of As_2S_3 per internal ampoule volume. The growth data for variation in diameter (e.g. nanowire or droplet) as a function of substrate temperature was fit to an exponential trendline with the form $y = Ae^{kx}$, where y is the structure diameter, $A = 1.25 \times 10^{-3}$, $k = 3.96 \times 10^{-2}$, and x is the temperature with correlation coefficient, $R^2 = 0.979$, indicating a thermally-activated process.

INTRODUCTION

Chalcogenide glasses are formed by combining chalcogen elements (S, Se, or Te) with Group IV or V elements (e.g., As). Arsenic sulfide (As_2S_3) is an important material belonging to this chalcogenide glass family. It is infrared (IR) transparent (700 nm-11.5 μm) and can be used in many IR applications such as sensors, waveguides, photonic crystals, and photolithography [1]. Recent studies [2] have revealed that, under specific
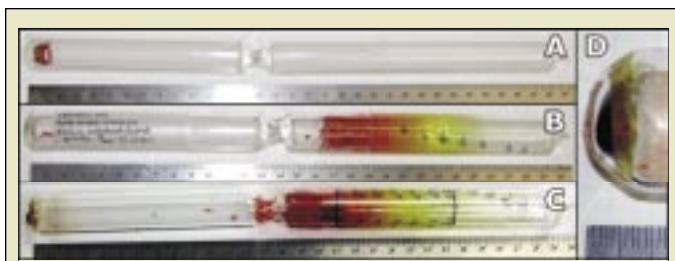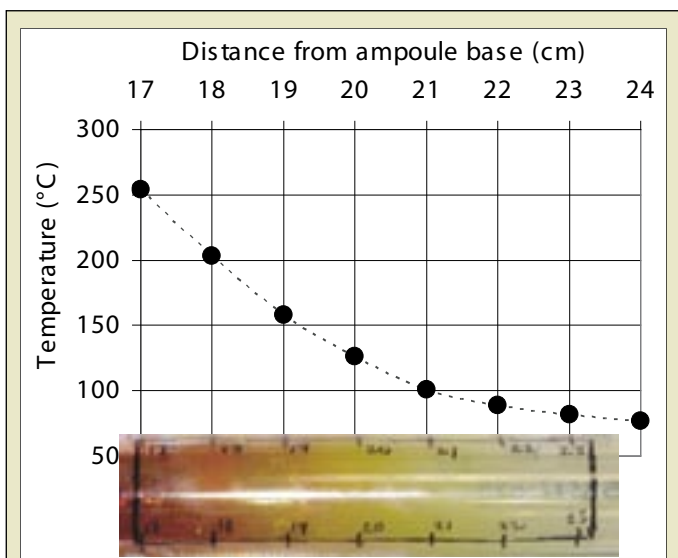
Figure 1-A, -B, -C, & -D: Examples of As2S3 deposition ampoules for nanowire growth. (A) As2S3 glass in the bottom of a fused quartz ampoule sealed at specified pressure pressure, before the heating process. (B) Picture of AEB1 following heat treatment. (C) Picture of AEB2 following heat treatment. (D) Close-up of the ampoule bottom of AEB2. The scale is in centimeters.

Figure 3. (A) SEM micrograph of nanodroplets from AEB1 at 94.1°C. (B) SEM micrograph of nanowires from AEB2 at 94.2°C. Initial ampoule pressure = 70 torr for both ampoules.
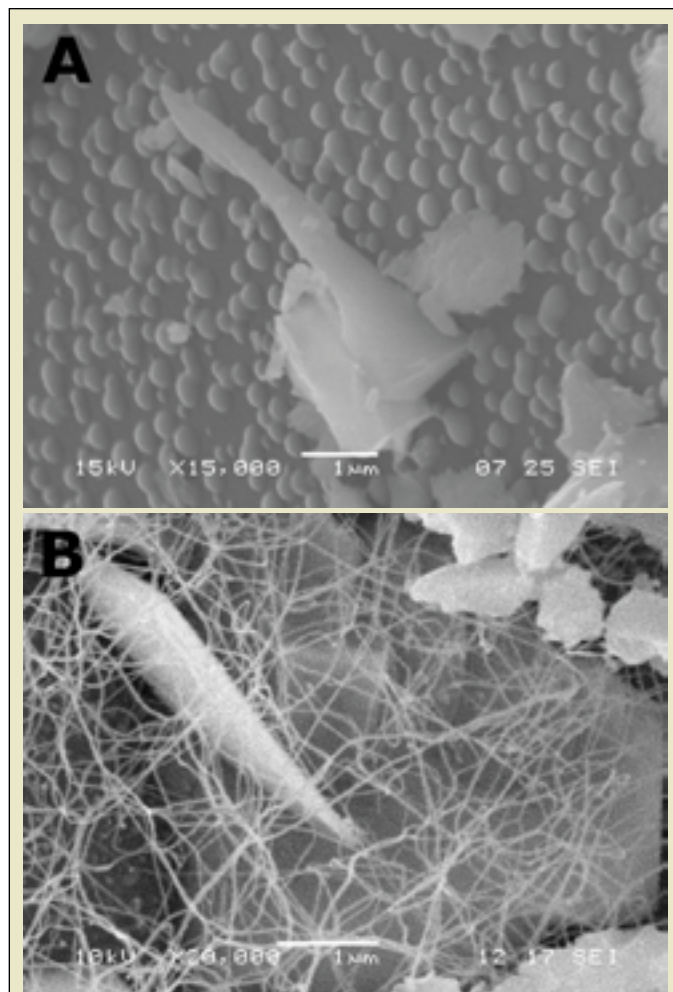
conditions, As_xS_y can form nanowires. These wires have diameters ranging from tens of nanometers to several hundred nanometers. They have been examined via transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), and Raman spectroscopy which revealed that they are amorphous in nature [2]. Their successful formation depends upon a variety of processing variables (i.e., pressure, temperature, duration of deposition, As_2S_3 glass purity level, quantity of As_2S_3 per internal volume and surface area of ampoule, substrate surface states, etc). As_2S_3 has also formed micro- and nanoscale droplet structures. The goal of the present study was to explore the effects of substrate surface chemistry and initial quantity of As_2S_3 glass on the formation of As_xS_y nanowires.

MATERIALS AND METHODS

The As_2S_3 used in this study was synthesized at PNNL. It was made by combining stoichiometric quantities of high purity elemental arsenic and sulfur (Alfa Aesar®, Ward Hill, MA) in evacuated and argon-purged fused quartz or borosilicate glass ampoules. The sealed ampoules were heated to a temperature between 480°C and 500°C and agitated in a rocking furnace (Deltech, Denver, CO) for up to 18 hours to ensure uniform mixing of the two components. After rocking, the ampoules were quenched in air down to approximately 200°C. The quenched glass was then annealed by placing

Figure 2. External substrate temperature profile of AEB2 (initial pressure of 70 torr) with accompanying picture of ampoule, demonstrating color variation with substrate temperature.

the ampoules in a furnace pre-heated to 170°C. The ampoules were held at that temperature for at least 2 hours, and then the furnace was turned off and allowed to slowly cool to ambient temperatures [2].

The experiments followed the general procedure established in previous work [2]. Deposition ampoules for nanowire growth were prepared from fused quartz tubes (GE 214 tubing, 1.9 cm ID, approximately 30 cm long internal volume of ~ 85 cm³). The surfaces of the interior walls (deposition substrate) were cleaned using an acid etching procedure with a solution of HF, HNO$_3$, and deionized water (DIW) in a 5:5:90 volume ratio, respectively, for 20 minutes. The ampoule was then rinsed with DIW and heat treated at 1000°C for 1 hour. This cleaning protocol had been selected from a number of different procedures, based on characterization data from atomic force microscopy (AFM – Nanoscope III, Veeco - formerly Digital Instruments) and x-ray photoelectron spectroscopy (XPS – PHI Quantum 2000). This cleaning protocol was termed "AEB" for acid-etched and baked.

After cleaning the deposition ampoule, a small mass of As_2S_3, usually about 1 gram (4.1×10^{-3} moles), was placed in it. A neck was created, ~ 13.5 cm from the bottom of the tube, by drawing the glass wall inward using an oxy-propane torch. The tube was then attached to a vacuum system, evacuated and back-filled with argon gas several times, and finally regulated to a pressure of 70 torr. The pressure was monitored with an

in-line pressure gauge during this process. Then the top of the deposition ampoule was sealed off using the torch. This created a closed system at the chosen starting pressure (Figure 1-A). The ampoule was instrumented with up to 17 K-type thermocouples (Omega Engineering, Inc., Stamford, CT) positioned at 1 cm intervals along the length of the deposition region of the ampoule. They were used to monitor the substrate temperature during the deposition process.

This ampoule was inserted into a secondary containment vessel (5 cm ID, fused quartz tube), and placed inside a top-loading furnace, with the upper region of the ampoule remaining outside the furnace. The ampoule was heated in the furnace at a rate of 5°C/min. to ~ 470°C, held at this temperature for 17.2 hours, and cooled back to room temperature at 5°C/min. The configuration of having the top half of the ampoule outside the furnace created a thermal gradient within the upper regions of the ampoule. The As_2S_3 glass evaporated from the bottom of the ampoule (the hottest region) and condensed along the upper wall of the ampoule at lower temperatures.

During the deposition process, a thin film of As_xS_y was deposited on the interior of the ampoule which was about 13 cm in length, starting from near the neck and continuing upwards (Figure 1-B, -C). The film varied in color from a deep red, at the bottom (warmer region), to pale yellow, at the top (cooler region). The detailed temperature range for these different regions was obtained using the data from the thermocouples (Figure 2). A portion of the ampoule within the colored thin film deposit region was sectioned from the ampoule, sputter coated with gold (Polaron Range SC7640, Quorum Technologies, England), and analyzed using an SEM (JEOL 5900 LV, Amherst, MA).

A plot was made of the thermal gradient (based on thermocouple data) along the wall of the ampoule where the sectioned piece was located (Figure 2). Also, etch marks were made on the specimen to designate the original thermocouple locations along the ampoule wall. The motorized stage on the SEM was used to measure distances between marks of known temperatures, and based on these distances and the thermal profile, the temperature at each point could be interpolated. Micrographs were taken of various microstructures, with an emphasis placed on wires and droplets. Their diameters were then semi-quantitatively measured in Adobe Photoshop CS˚. In this particular study, micrographs were taken from ~ 30 different temperature zones on a single sample, sometimes with multiple micrographs from a single area. Ten measurements were taken from each micrograph, and then these measurements were averaged together to give a single data point with a corresponding standard deviation.

Two experiments were performed to test the effect of the initial quantity of As_2S_3 per internal volume of the ampoule on nanowire formation in AEB cleaned deposition ampoules. The experiments were conducted using the same ampoule dimensions, initial pressure, cleaning method, and thermal treatment as described above, but with different amounts of As_2S_3 loaded into the ampoules. The first, AEB1, used $4.14×10^{-3}$ moles (1.02 grams) of As_2S_3, corresponding to $4.96×10^{-5}$ mol As_2S_3/cm^3. The second, AEB2, used $8.41×10^{-3}$ moles (2.07 grams) As_2S_3, corresponding to $1.01×10^{-4}$ mol As_2S_3/cm^3.

RESULTS

Experiment AEB1 produced nano/micro droplets only. The diameters of these droplets ranged from 175 ± 25 nm to 2.35 ± 0.61 µm, between the temperatures of 86°C and 156°C, respectively. The average standard deviation of the data points was 0.19 µm [3]. Figure 3-A shows a typical SEM micrograph from this experiment.

Experiment AEB2, on the other hand, produced a large number of nanowires as illustrated in Figure 3-B. Wire diameters ranged from 31 ± 6.1 nm to 86 ± 7.6 nm, between the temperatures of 84.0°C and 109.4°C, respectively. The average standard deviation for the wire diameter data was 7.7 nm. Microdroplets were also seen with diameters ranging from 2.0 ± 0.3 µm to 5.5 ± 0.3 µm, between the temperatures of 184.2°C and 220.6°C. The average standard deviation for the droplet diameter data was 1.8 µm. Figure 4 shows various SEM micrographs from AEB2, representing both wires and droplets. The wire diameter vs. temperature data fits an exponential trendline with an R^2 value of 0.912. The size (diameter) vs. temperature data for both wires and droplets also fits an exponential trendline, with an R^2 value of 0.979 (Figure 5). The trendlines for Figure 5-A and Figure 5-B fit the form, $y = Ae^{kx}$, where A and k are $9.32×10^{-4}$ and
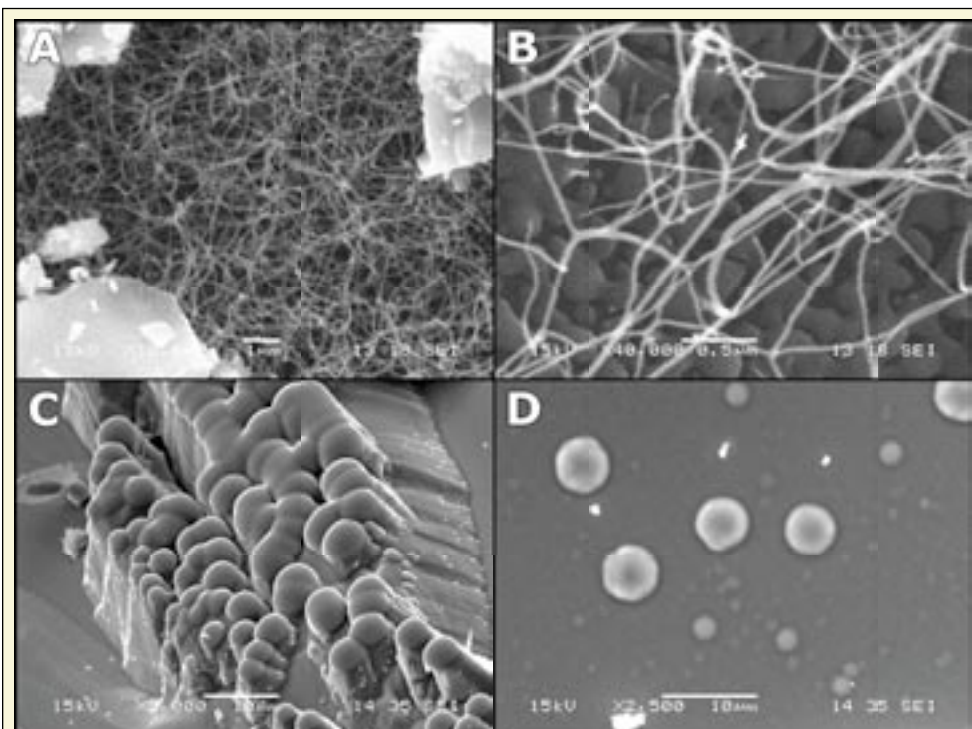
Figure 4. SEM micrographs of As2S3 deposits on the interior wall of AEB2. Micrographs A, B, C, & D were from different areas along length of ampoule wall (21.30, 22.00, 17.85, & 18.41 cm from bottom, respectively) with approximate substrate temperatures of 95.6°C, 89.0°C, 210.7°C, & 184.1°C, respectively.
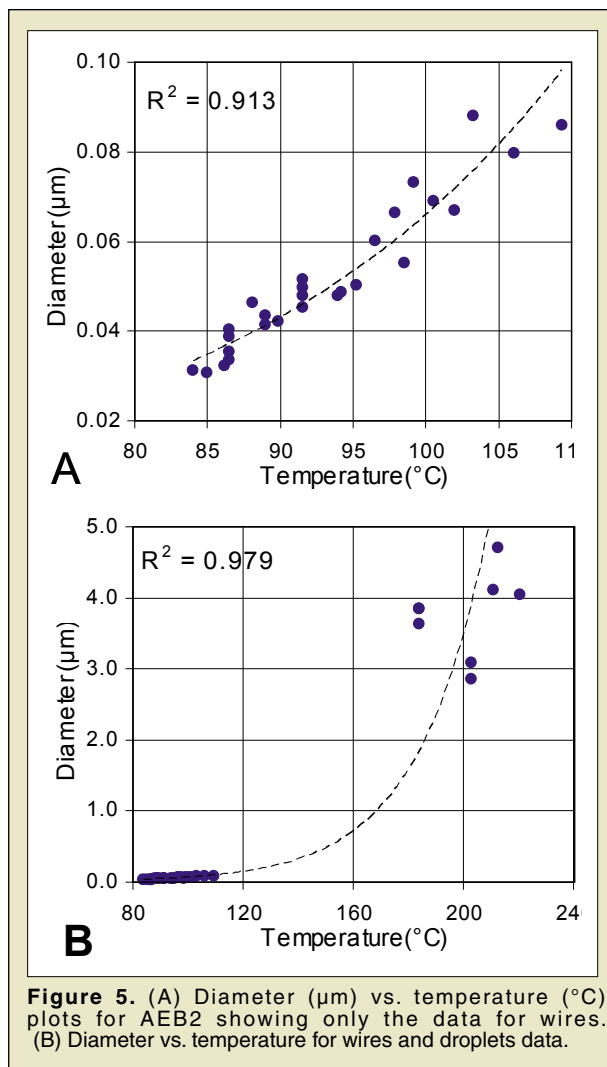
Figure 5. (A) Diameter (µm) vs. temperature (°C) plots for AEB2 showing only the data for wires. (B) Diameter vs. temperature for wires and droplets data.

4.26×10^{-2} for Figure 5-A, respectively, and 1.25×10^{-3} and 3.96×10^{-2} for Figure 5-B, respectively.

Additionally, there was a qualitative difference between the way the As_2S_3 deposited in AEB1 and AEB2. In AEB1, all the glass in the ampoule deposited on the upper walls (Figure 1-B). A couple of small pieces of As_2S_3 glass are visible near the bottom of the ampoule, but those appear to have fallen off the ampoule walls after the heating process. In AEB2, however, a small portion of the glass remained at the bottom of the ampoule after the evaporation-condensation process. The As_2S_3 also appears to have dripped down from the upper walls of the ampoule into the neck before it solidified (Figure 1-C, -D).

DISCUSSION

Experiments AEB1 and AEB2 had significantly different results, although the only parameter that was varied between the experiments was the quantity of As_2S_3 used per internal volume of the ampoule. Figure 6 shows a comparison of the diameter (size) vs. temperature plots for the two experiments, which highlights the difference between the structures formed. Mathematical curve fitting to the data suggests an exponential growth mechanism. A more systematic study is needed to determine the precise mechanism. In Figure 6, the trendlines fit the form $y = Ae^{kx}$ where

y is the structure diameter and x is the temperature. For AEB1, A and k are 1.42×10^{-2} and 3.34×10^{-2}, respectively, and for AEB2, A and k are 1.25×10^{-3} and 3.96×10^{-2}, respectively.
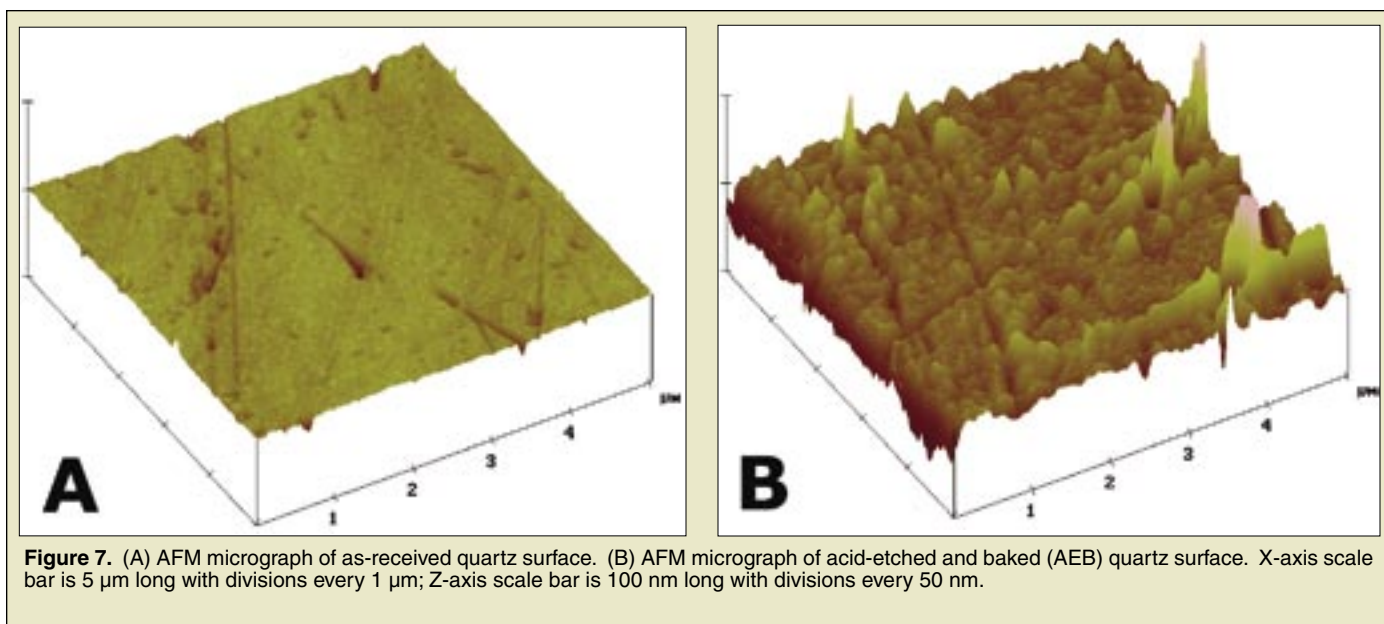
The differences between AEB1 and AEB2 could be due to a couple of factors. First, the pressure in AEB2 during the experiment was most likely higher than the pressure in AEB1. Even though both ampoules had the same initial pressure of 70 torr, AEB2 could have had up to twice the As_2S_3 vapor pressure during the deposition process, since it had twice the quantity of initial As_2S_3 per internal volume of the ampoule. This is consistent with the results from previous studies [2] which showed that nanowire formation was sensitive to pressure. Second, since the volume and internal surface area of the two experiments was approximately the same, the ratio of moles of As_2S_3 to the ampoule volume and surface area for AEB2 was double that for AEB1. In AEB1, there was no visible residual glass in the bottom of the ampoule, and the region of glass deposition did not extend down as far into the hotter regions of the ampoule as in AEB2. Thus, all of the As_2S_3 may have deposited quickly on the substrate walls during the AEB1 experiment and then no further structures would have formed due to depletion of the material supply. However, there was an apparent excess of As_2S_3 in the AEB2 experiment (glass in the bottom of the ampoule and near the neck) that possibly facilitated reflux and circulation of the As_2S_3 vapors, thereby providing sufficient material to allow nanowire growth to occur. Though we did not perform mass-balance, it is reasonable to postulate that the increase in the amount of available material would allow more interaction with the available surface, facilitating growth of complex microstructures (e.g. nanowires). Additional experiments are needed to verify this postulate.

The success of the second AEB2 experiment also showed that nanowires potentially can be deposited on a wider variety of silica surfaces than was previously known. This is a significant result, because in previous studies nanowires were only successfully formed on fused quartz ampoules that were cleaned using traditional laboratory cleaning methods (wash with water and rinse with DIW – "water-washed" surfaces) [2]. The effects of substrate surface modification are further discussed in detail elsewhere [3].

AFM analysis was used to conduct a detailed surface roughness characterization on an as-received fused quartz surface and on an AEB
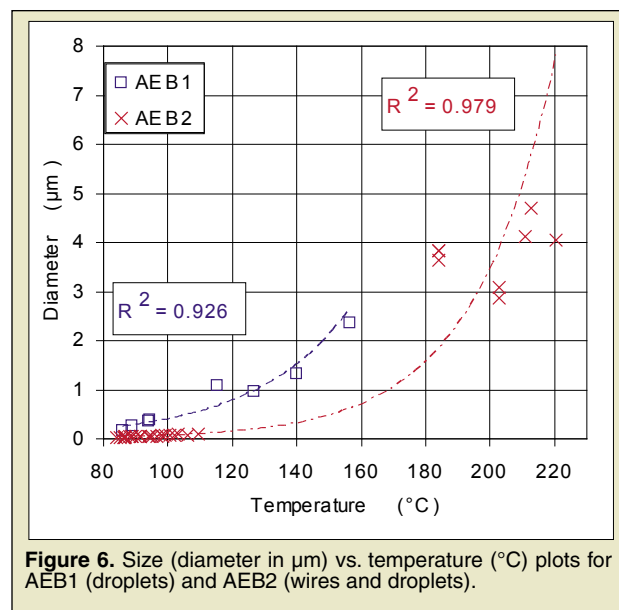
Figure 6. Size (diameter in µm) vs. temperature (°C) plots for AEB1 (droplets) and AEB2 (wires and droplets).

Figure 7. (A) AFM micrograph of as-received quartz surface. (B) AFM micrograph of acid-etched and baked (AEB) quartz surface. X-axis scale bar is 5 μm long with divisions every 1 μm; Z-axis scale bar is 100 nm long with divisions every 50 nm.

fused quartz surface (Figure 7). The results showed that AEB treatment significantly increased the roughness of the fused quartz surface. The Z range of the as-received sample, Figure 7-A, was 21.65 nm, whereas the Z range of the AEB sample, Figure 7-B, was 310.68 nm, increasing the peak-to-valley height difference by an order of magnitude. The root mean square (RMS) value also increased significantly, from 1.15 nm for the as-received sample to 9.06 nm for the AEB sample. In addition to the number of moles of As_2S_3 per available internal ampoule volume, the available deposition surface area also likely influences droplet/nanowire formation.

Additionally, XPS was performed on an as-received fused quartz sample and an AEB fused quartz sample. The results showed that the carbonaceous content of the surface was reduced from 21.9 ± 1.6 atomic % on the as-received sample to 0.7 ± 0.1 atomic % on the AEB sample, a decrease of nearly two orders of magnitude. Therefore, the AEB surface contains significantly less carbonaceous contamination than the as-received sample. It is likely that this difference also affects the way As_xS_y deposits on an AEB surface versus a water-washed one. Further detailed investigation will be needed to determine the precise roles of carbonaceous contamination as well as molar surface area in the formation of nanowires and other features.

CONCLUSION

Several main conclusions can be drawn from this study. First, nanowire formation on an AEB surface has been demonstrated, which is a new finding. Second, the initial quantity of As_2S_3 has been shown to be a crucial variable in nanowire formation on AEB surfaces. Under identical initial conditions, there is a minimum quantity of As_2S_3 required for nanowire synthesis, below which nanowires do not form. Third, the growth of nanowires and nano/micro droplets as a function of substrate temperature has been fitted to an exponential curve. And finally, the surface chemistry and roughness of AEB cleaned fused quartz surfaces have been characterized and shown to create a significantly cleaner, yet rougher surface than initially present. In summary, we have presented a process that can be replicated more consistently and accurately which is expected to lead to standardized nanowire synthesis, a major step towards commercial production.

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