

Bulk synthesis of a-Si_xN_yH and a-Si_xO_y straight and coiled nanowires†

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Received 29th September 2003, Accepted 13th November 2003
First published as an Advance Article on the web 8th January 2004

We report the bulk synthesis of hydrogenated, amorphous Si_xN_y and Si_xO_y nanowires using pools of molten gallium as the solvent medium and microwave plasma consisting of silane in nitrogen and silane in oxygen respectively. High densities of multiple nanowires nucleated and grew from molten gallium pools. The resulting nanowires were tens of nanometers in diameter and tens of microns long. Electron energy loss spectroscopy (EELS) and Fourier transform infra-red (FTIR) spectroscopy showed that the silicon nitride nanowires are hydrogenated amorphous silicon nitride (a-Si_xN_yH). The results of energy dispersive X-ray spectroscopy (EDS) yielded N : Si and O : Si ratios less than the stoichiometric composition of silicon nitride (Si₃N₄) and silica (SiO₂). Studies on the chemical stability and refractive index (RI) measurements demonstrate a-Si_xN_yH nanowires are potential candidates for use as etching masks in nanoscale lithography, and as high index materials in optical coatings.

Introduction

Silicon nitride and silicon oxide are technologically important materials that will find applications in nanometer scale optical, electronic, and optoelectronic systems.^{1,2} The Si–N–O systems provide materials that have tunable refractive indices (RI) over a wide range. For example, the RI could be varied from 4.0 for silicon to 1.97 for stoichiometric silicon nitride to 1.46 for silicon dioxide. Nanowires of silicon–oxygen–nitrogen compounds with different compositions could be used in making thin film stacks for use in anti-reflective (AR) coating applications.³ In addition the superior chemical resistant properties of the silicon nitride nanowires could potentially lead to nanometer scale lithographic features for circumventing the size limitations associated with optical lithography.

Silicon oxide nanowires could provide a better alternative compared to the currently used nanoparticle dispersions for low-refractive index materials in AR coatings with improved mechanical stability.⁴ In addition, the amorphous silicon oxide nanowires have been shown to exhibit stable, bright blue light.⁵ Thus, the silicon oxide nanowires are potential candidates for applications in optical and optoelectronic devices such as waveguides and high-resolution optical heads of near-field scanning optical microscopes.⁶

Many optical applications require that stacks of thin films with different refractive indices be deposited onto a variety of substrates at temperatures less than 200 °C. Recently, it was shown that one could tune RI values of thin films by dispersing nanoparticles into polymer matrices at low temperatures.⁷

However, nanoscale materials with the desired high RI properties are not readily available, except for crystalline titania. In this regard, the bulk syntheses of nanowires of silicon nitride, silicon oxynitride and silicon oxide compounds are of interest.

Most of the current methods for synthesis of nanowires utilize catalyst clusters to template one-dimensional growth selectively.^{8–10} Many of the current methods are just variations of the original concept by Wagner and Ellis¹¹ in terms of the catalyst type and the method used for generating nanometer scale catalyst clusters. Recently, we presented a different concept in which multiple nanowires nucleate and grow by basal attachment from pools and thin films of low-melting metal melts.¹² The low-melting metals are not known for their catalytic ability toward dehydrogenation reactions. So, we found it necessary to activate the gas phase for solute dissolution. The gas phase activation can be done using a variety of methods including hot-filaments, plasmas and thermal means. Earlier, we demonstrated this technique with silicon nanowire growth using hydrogen plasma over silicon substrates covered with gallium,¹² and then later using silane–hydrogen plasma over a gallium covered non-silicon substrate.¹³ We have also demonstrated this concept with the direct growth of gallium nitride nanowires at high temperatures around 900 °C,¹⁴ and gallium oxide nanowires at lower temperatures, around 500 °C,¹⁵ on quartz substrates. In this paper, we describe the development of this technique for use with multiple solutes provided *via* the gas phase using appropriate mixtures of silane, nitrogen and oxygen over molten gallium for synthesizing silicon nitride and silicon oxide nanowires. See the schematic in Fig. 1.

Experimental

The nanowire growth experiments were performed by exposing a quartz substrate covered with a molten gallium film to microwave plasma containing a mixture of 2% SiH₄–H₂ in N₂ for silicon nitride nanowires, and 2% SiH₄–H₂ in O₂ for silicon

† Electronic supplementary information (ESI) available: Movies taken using a microscope. File RI19, shows a white fringe (Becke Line), which surrounds the particle, shift into the particle when the lens is moved farther away from focus. This indicates that the RI of the particle is greater than the surrounding calibration solution (RI = 1.9). Files RI21 and RI23 show the Becke line moving from the particle into the surrounding indicating that the RI of the particle is lower than its surrounding RI of 2.1 and 2.3 respectively. See <http://www.rsc.org/suppdata/jm/b311887h/>

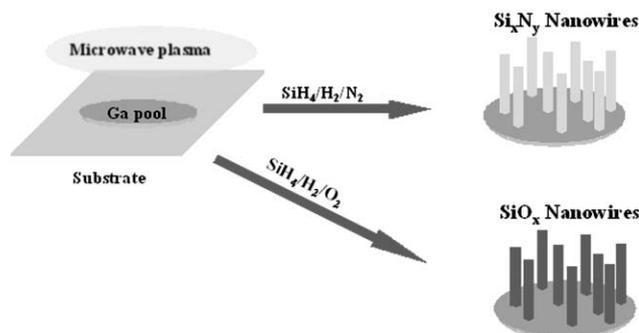


Fig. 1 Direct control of the nanowire composition by gas phase manipulation.

oxide nanowires, respectively. The results did not depend upon the type of substrate used as long as the substrate material was inert to molten gallium at temperatures around 600 °C. The nanowire growth experiments were performed for durations ranging from 15 min to 3 hours over a range of process conditions: 500 to 1100 W microwave power, and 10 to 50 Torr pressure, and 0.5–50% N₂ or O₂ in 2% SiH₄–H₂. The substrate temperature was determined using an infrared pyrometer to be approximately 550 °C for a microwave power of 750 W, 30 Torr pressure and 40 sccm N₂ in 100 sccm 2% SiH₄–H₂. The as-synthesized nanowires were analyzed for morphology and composition using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) and Fourier transform infrared spectroscopy (FTIR) respectively. Transmission electron microscopy (TEM), and X-ray diffraction (XRD) analysis of the sample, not presented here, indicated that the nanowires are amorphous. Chemical stability experiments were performed by boiling 2 M KOH for 10 minutes on a silicon substrate followed by imaging using an atomic force microscope (Park Scientific). The refractive indices (RI) of the nanowire samples were measured using the Becke Line technique with the help of liquid standards (obtained from Cargille Laboratories, NJ, USA) for RI values up to 2.3. See reference 16 for a standard description of Becke line experimental techniques.

Results and discussion

The experiments using the silane and nitrogen mixture diluted in hydrogen resulted in bulk nucleation and growth of silicon nitride (Si_xN_y) nanowires from the gallium melt (see Fig. 2). The results obtained for the growth of Si_xN_y nanowires are similar to those obtained with silicon nanowires,¹³ *i.e.*, multiple wires nucleated and grew from larger gallium droplets. Although, the low magnification images show the nanowires to be straight, higher magnification images reveal that the nanowires are in fact coiled with regular intervals like springs, as shown in Fig. 3(a). The occurrences of the coiled morphology seem to prevail over the entire sample and are not limited to a particular location. In addition, the individual nanowires growing from a gallium droplet seem to converge, and grow together as a bundle as indicated in Fig. 3(b). We suspect that the constraints caused by the faster growth rate at the basal point (indicated as 'A') in Fig. 3(b) and the slower moving bundle (indicated as 'B') in Fig. 3(b) force the wires to coil like a spring during growth. McIlroy *et al.*¹⁷ reported the growth of amorphous boron carbide nanosprings using catalyst cluster templated growth and hypothesized that they resulted from surface tension interactions between the growing nanowires and the catalyst particle. Also, Zhang *et al.*,¹⁸ reported the synthesis and characterization of helical amorphous silica nanosprings, and suggested an anti-VLS mechanism for the

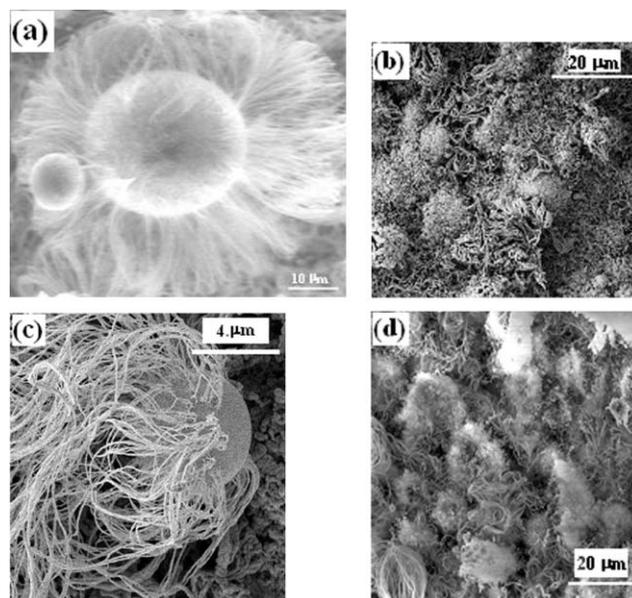


Fig. 2 SEM micrographs of silicon nitride nanowires in a typical experiment. (a) and (c) Multiple silicon nitride nanowires grown from a micron sized gallium droplet exposed to plasma containing silane and nitrogen. (b) and (d) Low magnification micrographs showing a high density of Si_xN_y nanowires over a large area. The experimental conditions were 700 W power, 30 Torr pressure, 50 sccm of 2% silane in hydrogen and 100 sccm of nitrogen and a duration of 3 hours.

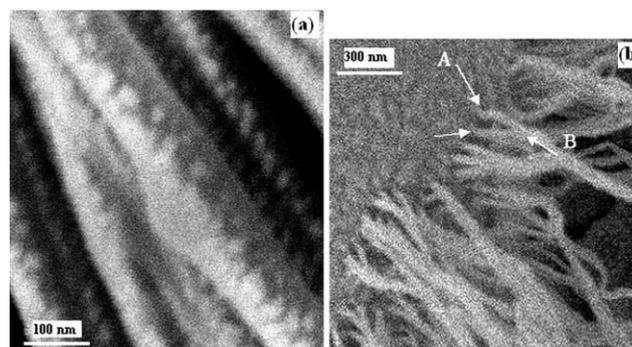


Fig. 3 (a) SEM micrograph showing the coiled morphology of Si_xN_y nanowires. (b) SEM micrograph showing the location of individual nanowire nucleation on the molten gallium surface (denoted as 'A') and the location of bundles of nanowires (denoted as 'B').

formation of these novel structures. In this regard, our observations of coiled wire growth of amorphous silicon nitride, using a method that does not use catalyst clusters, are interesting and quite unique.

Fig. 4 shows a typical AFM topographical map of nanowire bundles on a silicon substrate after 10 minutes of etching using 2 M KOH at 90 °C. The underlying silicon substrate was etched as indicated by the roughness while the nanowire bundle was not etched. These results suggest that the a-Si_xN_yH nanowires could be used as nanometer scale, etch resistant masks for nano-lithography.

Fig. 5 shows the EELS spectra taken from a 15 nm thick silicon nitride nanowire. The spectrum clearly shows the Si–L_{2,3} edge at 104 eV and the N–K edge at 401 eV which confirms that the nanowires are composed of silicon and nitrogen. The Si–L_{2,3} edge at 104 eV indicates Si–N covalent bonding in the nanowire.¹⁹ The absence of the O–K edge (at 540 eV) in the EELS spectrum, as indicated in Fig. 5(b), confirms the absence of oxygen in the nanowire.²⁰ The nanowires did not exhibit any electron diffraction spots or rings resulting from nanocrystallinity thus indicating amorphous character. The XPS spectrum in Fig. 6 was obtained using a bulk quantity of the sample

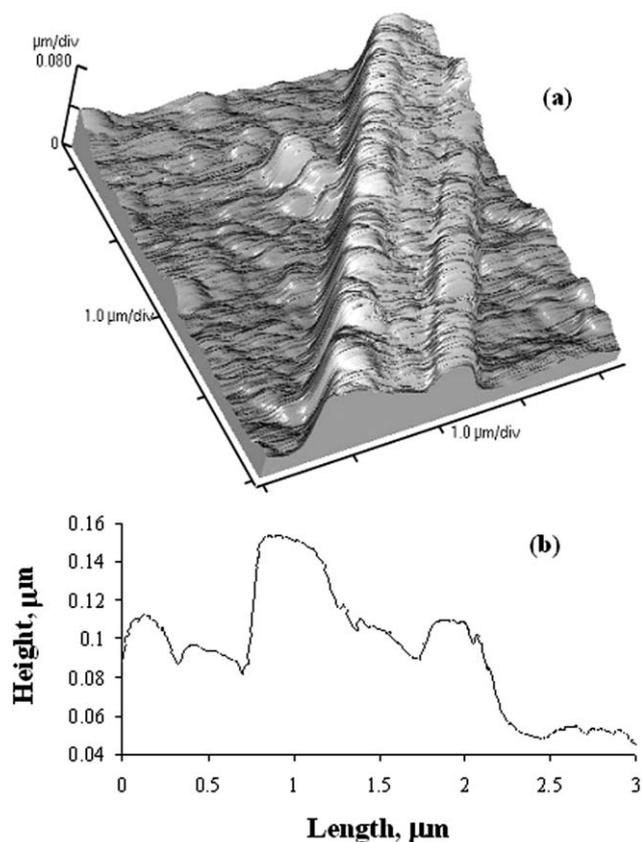


Fig. 4 (a) AFM micrograph and (b) line profile of a Si_xN_y nanowire on a silicon substrate showing the etched rough silicon surface. The etching experiment was performed with boiling 2 M KOH for 10 minutes.

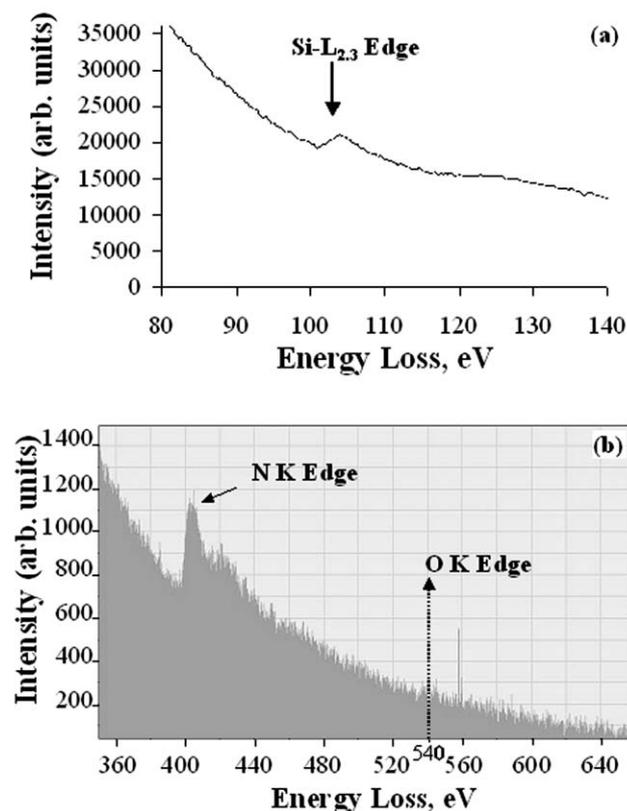


Fig. 5 (a) EELS spectrum taken from an individual nanowire 20 nm thick showing the Si- $L_{2,3}$ edge. (b) EELS spectrum taken from the same nanowire as in (a), showing the N-K edge and the absence of an oxygen shift.

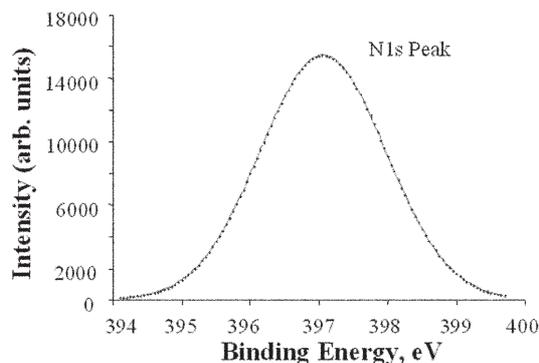


Fig. 6 XPS spectra of the SiN nanowires shows the binding energy of the N 1s peak corresponding to a Si-N single bond.

(3 mm \times 3 mm in areas) and shows a peak due to N 1s at 397 eV indicating Si-N bonding.

The IR spectrum of the Si_xN_y nanowires exhibited a broad peak from 1300 to 700 cm^{-1} as shown in Fig. 7. Upon deconvolution, the broad peak yielded a total of 8 symmetric peaks at 1220, 1161, 1083, 1040, 1002, 947, 879 and 781 cm^{-1} . All of these deconvoluted peaks are shown in Fig. 7. The Si-N-Si stretching band at 947 cm^{-1} and the N-Si-N stretching band at 879 cm^{-1} can be seen, and compare well with the IR spectra obtained from the commercially available amorphous silicon nitride powder (obtained from Nanostructured & Amorphous Materials, Inc., NM, USA). The peaks observed between 1050 to 960 cm^{-1} may be due to the presence of variations in the different local environments of Si-H bonds within the amorphous network. In addition, the spectrum of the nanowires shows a relatively small Si-O stretching band between 1100–1080 cm^{-1} compared to that obtained with the commercial nanoparticle sample, suggesting lower oxygen incorporation into our nanowire samples relative to the as-received commercial nanopowder sample. The overall IR analysis suggests that the synthesized, amorphous silicon nitride nanowires samples are hydrogenated.

Although further investigation is certainly needed using large quantities of samples, our initial investigations into the RI properties of a- $\text{Si}_x\text{N}_y\text{H}$ nanowire agglomerates using the Becke Line method¹⁶ suggested RI ranging from 1.9 to 2.3, for samples synthesized under different conditions. The observed variations in the RI of the synthesized nanowire samples may be due to variations in their composition, *i.e.*, Si : N ratio. Systematic investigations are currently being performed to

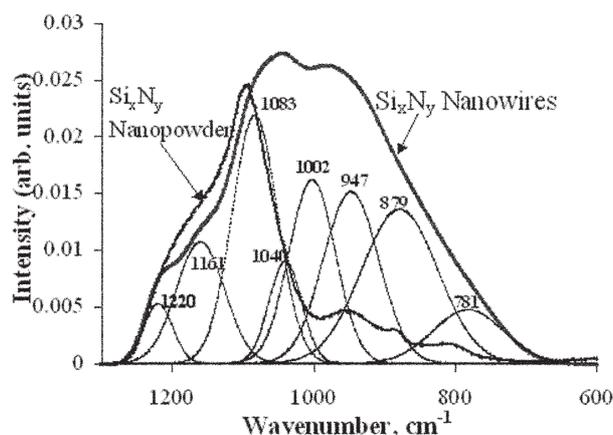


Fig. 7 IR spectrum of a- Si_xN_y nanowires shows very little Si-O vibration as compared to commercially obtained amorphous silicon nitride powder, while the nanowires show an enhanced peak between 1050–850 cm^{-1} which may correspond to Si-N-Si, N-Si-N and N-H stretching. The symmetric deconvoluted peaks are depicted along with their corresponding wavenumbers.

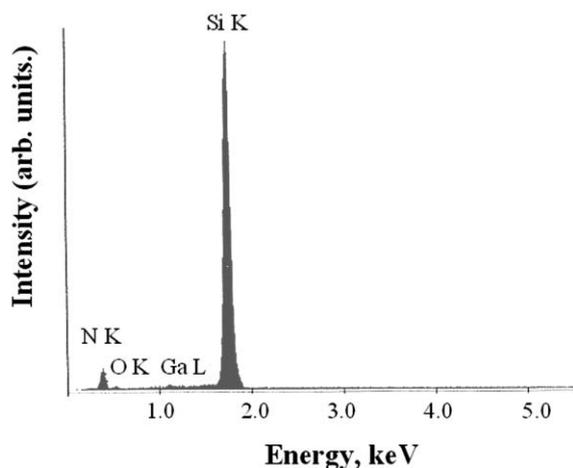


Fig. 8 EDS spectrum of the as-synthesized nanowires shows very little oxygen content and a Si : N ratio of approximately 1.

correlate the Si : N ratio measured using a combination of techniques (Becke line, EDS, IR and EELS) and process parameters (MW power, silane : nitrogen ratio and substrate temperature). The commercial titania nanopowders (Nanostructured and Amorphous Materials Inc., NM) showed a RI value between 1.5 and 1.7 for the as-received rutile phase and a RI value between 1.9 and 2.1 for the as-received anatase phase. Using the same technique, the RI values for the commercially available α - Si_3N_4 nanopowder were significantly lower than 1.9. Our amorphous silicon nitride nanowires exhibited a high RI value probably due to the higher silicon content (Si : N > 0.75 in Si_3N_4).²⁰ This observation is clearly consistent with the presence of hydrogen (Si–H bonds) noted in the IR spectrum analysis. Possibly, the composition of the nanowires in the absence of oxygen would vary from fully hydrogenated amorphous silicon nanowires to hydrogenated, amorphous silicon nitride. However, it has been difficult to quantify the Si : N ratio in the nanowires using EDS in a scanning electron microscope. See the EDS spectrum in Fig. 8. In general, the ratio of Si : N of different samples prepared under different processing conditions is estimated to range from 0.75 to 1.25.

The experiments performed using the silane and oxygen mixture diluted in hydrogen plasma resulted in SiO_x nanowires.

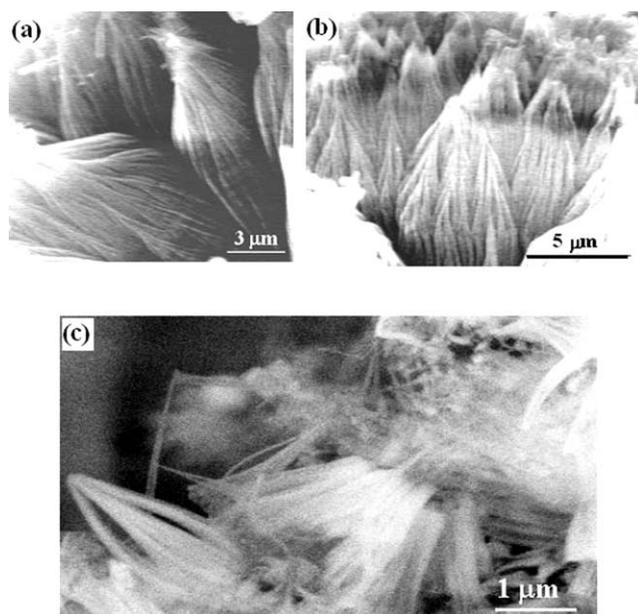


Fig. 9 (a)–(c) The SEM micrographs show high density of silicon oxide nanowires nucleated and grown from large pools of molten gallium.

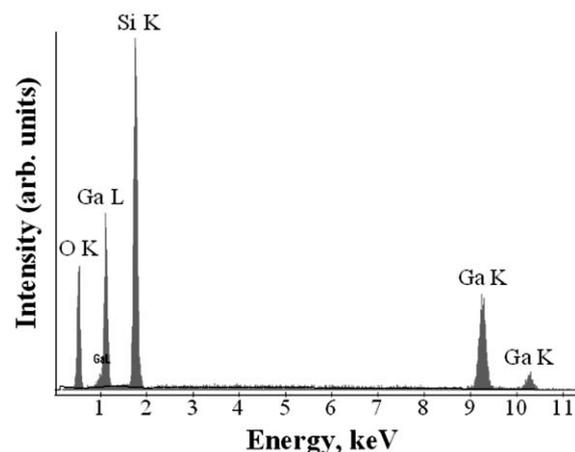


Fig. 10 EDS spectrum of the as-synthesized nanowires. The gallium peaks arise due to the large quantity of gallium in the vicinity of the nanowires.

See Fig. 9 for SEM images. The results with silicon oxide nanowires are similar to those of the α - Si_xN_y nanowires, *i.e.*, a high density (in the order of 10^{12} cm^{-2}) of wires nucleate and grow selectively from large gallium pools. The nanowires are typically less than 70 nm in diameter and several tens of microns long. Fig. 10 shows the EDS spectrum of the as-synthesized nanowires. The O : Si atomic ratio was estimated to be between 0.2 and 1.4 for samples synthesized under different processing conditions. The O : Si ratio measured using EDS could have been influenced by the signal from the underlying quartz substrate.

In our earlier reports,¹³ the experiments with gallium pools exposed to silane plasma resulted in the bulk nucleation and growth of silicon nanowires. The formation of nanometer scale nuclei of silicon from molten gallium in which silicon is dissolved can be rationalized using the binary (Ga–Si) phase diagram. However, no information is available on ternary phase diagrams involving gallium, silicon and nitrogen or oxygen. The exposure of gallium covered silicon substrates to MW plasma consisting of hydrogen diluted in nitrogen resulted in the growth of elemental silicon nanowires.¹² The resulting silicon nanowires were free of nitrogen indicating no nitridation had occurred. Under similar conditions, direct nitridation of bulk silicon was found to be low.⁴ The high N : Si ratio observed in α - Si_xN_y :H nanowires and the high growth rates indicate that the *in situ* nitridation of silicon nanowires is not the operative mechanism here. Similarly, the dissolution of nitrogen in molten gallium at 400–600 °C and 30 Torr pressure is expected to be small ($<10^{-4}$ at%) even in the presence of atomic nitrogen in the gas phase.²¹ In fact, it is necessary to use temperatures as high as 900 °C to dissolve atomic nitrogen at substantial concentrations in molten gallium for gallium nitride crystal synthesis.¹⁴

In summary, the ease with which amorphous silicon nitride nanowires nucleate and grow from molten gallium pools suggests that the dissolution of silane and nitrogen gas is fast and selective at the molten gallium surface. Possibly the dissolution of silicon and nitrogen could occur through Si–N and Si–NH type gas phase species. However, a set of preliminary equilibrium gas phase calculations did not indicate the presence of either SiN or SiNH species in the gas phase at temperatures lower than 600 °C. Similar results of high nucleation densities and fast growth rates for silicon oxide nanowires from molten gallium pools are also surprising. In neither case is the dissolution mechanism understood. In the case of silicon nitride nanowires, the chemisorption of hydrogen and/or NH_x species on the molten gallium surface possibly increased the formation and the dissolution of silicon–nitrogen complexes

into the bulk gallium pool. However, further analysis is necessary to verify the above-proposed hypothesis for the dissolution mechanism.

Conclusions

The experiments with silane–nitrogen and silane–oxygen gases diluted in hydrogen plasma over molten gallium pools resulted in bulk nucleation and growth of amorphous silicon nitride and silicon oxide nanowires, respectively. The growth of both silicon nitride and silicon oxide on molten gallium surfaces was found to be highly selective. The composition of the resulting silicon nitride nanowires was found to be hydrogenated $a\text{-Si}_x\text{N}_y$, with the x/y ratio ranging from 0.75 to 1.25. The RI of the $a\text{-Si}_x\text{N}_y$ nanowire samples were determined to be greater than 1.9. The results with both silicon nitride and silicon oxide nanowires suggest that one can easily synthesize a variety of Si–N–O:H nanowires with different compositions for tuning the optical properties (refractive index) by varying the activated gas phase composition over the molten gallium surface at relatively modest temperatures between 400–500 °C.

Acknowledgements

The authors greatly appreciate partial financial support from NSF through a CAREER grant (CTS 9876251) and an infrastructure grant (EPS 0083103). The authors also acknowledge Dr Steve Harfenist (U of L) for his help with AFM.

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