Temperature-dependent Electrodeposition of Crystalline Si Prepared by an Electrochemical Liquid-Liquid-Solid Growth Process

by Junsi Gu

Crystalline group IV semiconductor materials are essential components in microelectronics, solar cells, and sensor applications.[1] Conventional large-scale production of crystalline Si relies on energy-demanding processes necessary to chemically reduce precursors at elevated temperatures.[2] Exploration of alternative non-energy-intensive synthetic methods is thus critical to reduce the massive energy input in the currently available production strategies. Electrochemical deposition provides a scalable, easy-to-access option for producing semiconductor materials. Reports have demonstrated the utilization of electrodeposition in preparation of group IV semiconductors from molten salts[3] or non-aqueous solvents,[4] yet the challenges remain due to high crystallization barriers of covalent semiconductors to yield crystalline group IV semiconductor as-deposited at low temperature.[5]

Our group has recently demonstrated an electrochemical liquid-liquid-solid (ec-LLS) process to electrochemically deposit crystalline Si nanocrystals under bench-top conditions at temperatures compatible with aqueous and organic solvents.[6] As depicted in Fig 1a, the key innovation in our strategy involves the use of liquid Ga electrodes functioning both as conventional cathodes and crystallization solvents for crystal growth. In our approach, elemental Si is first electrochemically reduced from its high-valence precursor $SiCl_4$ at the liquid Ga surface, followed by dissolution into the liquid metal to form a Si-Ga alloy. Continuous reduction and dissolution cause the alloy to reach supersaturation, leading to phase segregation that yields Si nano-crystals. In such a process, the temperature dictates both the nucleation and crystal growth steps by affecting the alloy saturation point and crystal growth kinetics. This report will test the hypothesis that growth temperature has a primary influence on crystallite size and deposit morphology.

Figure 1b shows the cyclic voltammetric response of Ga(l) electrodes at room temperature in a propylene carbonate (PC) solution of 0.05 M $SiCl_4$ and 0.2 M tetrabutylammonium chloride (TBAC), highlighting the cathodic wave that indicates the reduction of $SiCl_4$ at -2.0 V *vs.* Pt quasi-reference electrode (QRE) before the onset of solvent decomposition at ca. -3.2 V. No such feature was observed with the absence of dissolved $SiCl_4$.

Temperature-dependent electrodeposition was carried out potentiostatically at -2.5 V *vs.* Pt QRE at 120, 140, and 160 °C, respectively in the PC solution of 0.05 M $SiCl_4$ and 0.2 M TBAC. For Si deposits obtained at 120 and 140 °C, the scanning electron micrographs (Fig. 2a, 2b) show that the morphology was dominated by faceted nanocrystals, indicating the crystalline nature of the product. Statistics analysis (N = 50) of the crystal sizes (Fig. 2c) reveals an increase in the average crystal size from 0.25 to 0.36 μm^2 and broadening in the distribution as the growth temperature increases. Further increase in the growth temperature to 160 °C results in the emergence of high-aspect-ratio morphology (Fig. 2d). Elemental analysis based on energy dispersive X-ray spectroscopy (Fig. 2e) indicates the deposit contains primarily Si with a small contribution from Ga and O. The results collectively indicate that growth temperature influences not only the crystallite size but also the deposit morphology. Further study is required to understand the driving forces for different growth morphology to provide better control of the products through ec-LLS.

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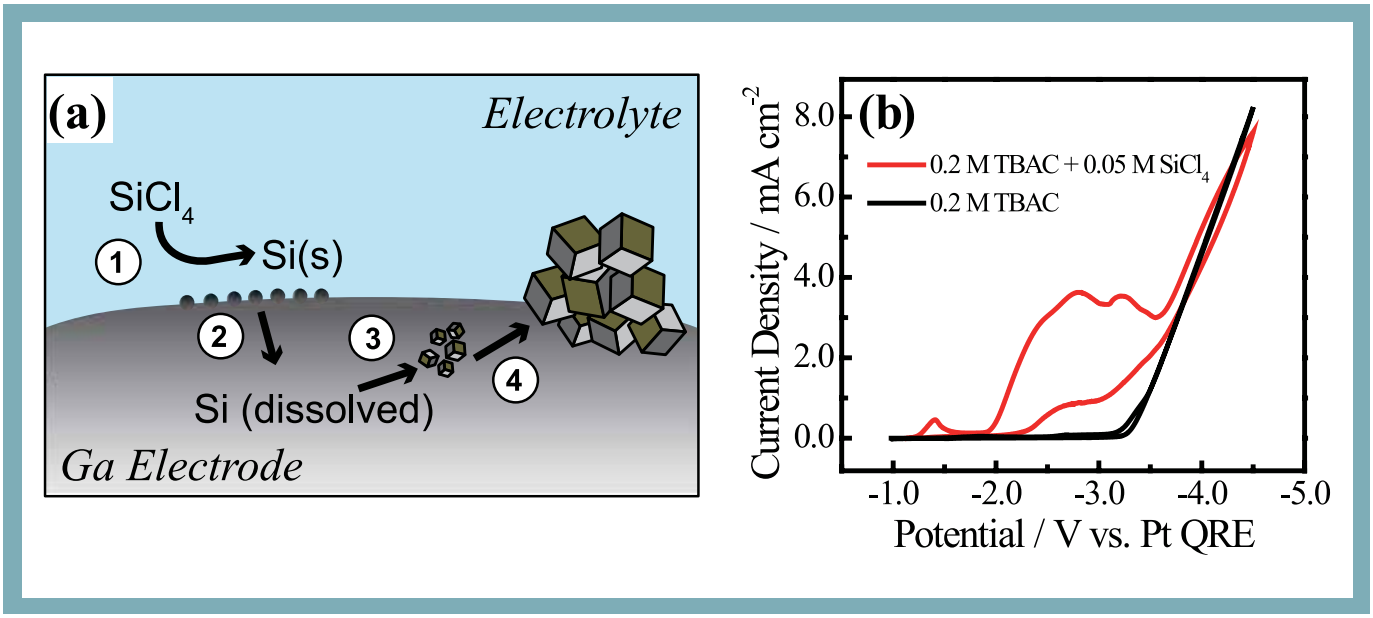

FIG. 1. *(a) Schematic depiction of the electrochemical liquid-liquid-solid process. (b) Cyclic voltammetric response of liquid Ga electrodes at room temperature in a propylene carbonate solution containing 0.2 M tetrabutylammonium chloride with (red) and without (black) dissolved 0.05 M $SiCl_4$.*

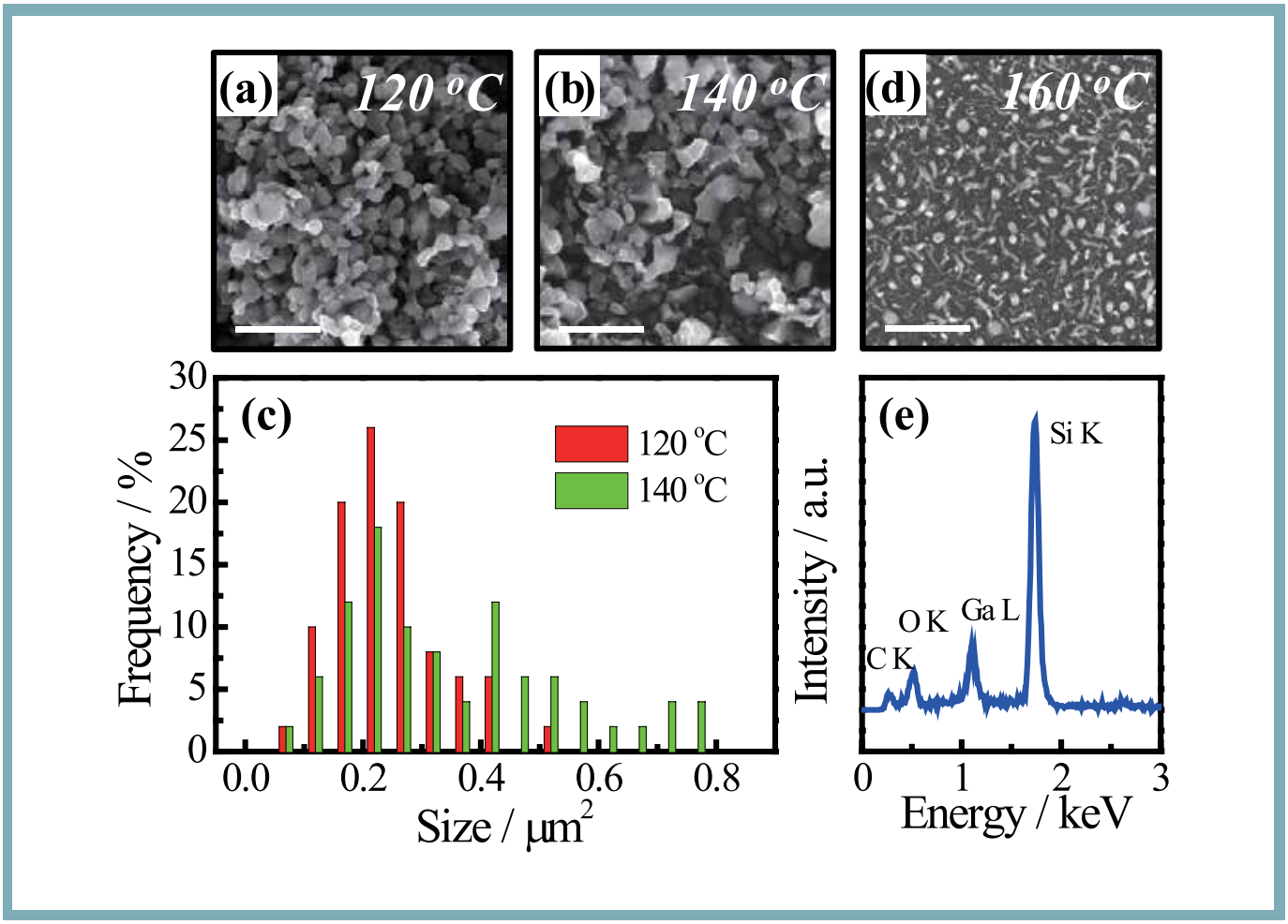

Fig. 2. *Scanning electron micrograph of Si prepared by ec-LLS process at (a) 120 °C and (b) 140 °C. (c) Histogram showing size distribution of Si crystallites observed in (a) and (b). (d) Scanning electron micrograph of Si prepared by ec-LLS process at 160 °C. (e) Energy dispersive X-ray spectrum of the deposits observed in (d). All electrodeposition was performed in a propylene carbonate solution containing 0.2 M tetrabutylammonium chloride and 0.05 M $SiCl_4$ at -2.5 V vs. Pt QRE for 1 hr. Scale bar: 2 μm.*

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References

1. K.-Q. Peng and S.-T. Lee, *Adv. Mater.*, **23**, 198 (2011).
2. C. S. Tao, J. Jiang, and M. Tao, *Sol. Energy Mater.*, **95**, 3176 (2011).
3. S. K. Cho, F.-R. F. Fan, and A. J. Bard, *Angew. Chem.*, Int. Ed., **51**, 12740 (2012).
4. Y. Nishimura and Y. Fukunaka, *Electrochim. Acta*, **53**, 111 (2007).
5. U. Köster, *Physica Status Solidi (A)*, **48**, 313 (1978).
6. J. Gu, E. Fahrenkrug, and S. Maldonado, *J. Am. Chem. Soc.*, **135**, 1684 (2013).