Molecular Sensing with Ultrafine Silver Crystals on Hexagonal Aluminum Nitride Nanorod Templates

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Group III−nitride semiconductors are automatic choices for nanoscale optoelectronic device materials working over a wide range of wavelengths. A recent report of an infrared band gap for indium nitride (InN)[1] and the deep ultraviolet band gap of aluminum nitride (AlN) stretches the limit of their optical domain. The ongoing furor about the fundamental gap of InN and the continued development of gallium nitride (GaN) as a light-emitting diode material has involved intense scientific work on these materials. AlN was known for its high thermal conductivity, hardness, and chemical inertness,[2] and it provides a better lattice-matched substrate for GaN deposition. Of late, scientists working in the nanoscale regime seem to realize that AlN, among this very important group III−nitride family, is being left behind. As a consequence, we have seen reports, although few, of one-dimensional AlN materials, such as AlN nanotubes,[3,4] nanowires,[5] and nanobelts,[6] which have been successfully developed. The synthesis of defect-free nanostructures and their characterization is undoubtedly the key step in realizing any optoelectronic device in the future. However, we need not limit ourselves to optoelectronic devices in an effort to utilize the whole range of band gap that these group III−nitrides have to offer. This paper reports the synthesis of hexagonal AlN (h-AlN) nanorods and their use as a template for vacuum deposition of silver (Ag) nanocrystals aiding in surface-enhanced Raman scattering[7] (SERS). The SERS technique, with sufficient enhancement[8] of the Raman signals even at room temperatures, is posing a serious challenge to the conventional low-temperature fluorescence spectroscopy used in analytical studies.

Quasi-aligned h-AlN nanorods were synthesized by vaporizing pure Al powders under flowing ammonia gas at 1200 °C and subsequent condensation and further nitridation of the vapor on silicon substrates coated with a thin layer of gold. This process is referred to as vapor transport and condensation.[9] The Al powders and the gold-coated Si substrates were placed upstream and downstream, respectively, with respect to the NH₃ flow in a ceramic boat held in a tubular furnace. The furnace temperature was ramped up to 1200 °C and kept there for 30 min. Upon cooling, a whitish product was obtained on the Si substrates. Scanning electron microscope (SEM) images of the deposit reveal them to be sharply faceted quasi-aligned nanorods with a hexagonal cross section. Figure 1a shows the SEM (JEOL JSM 6700F) images of the as-grown AlN nanorods with diameters of 100−300 nm and lengths of about 0.5−1 μm. The XRD spectrum (spectrum A of Figure 1c) of the as-grown AlN nanorods shows strong signatures of h-AlN phases ((100), (002), and (101)) (JCPDS file no. 25-1133), along with unreacted pure Al (JCPDS file no. 04-0787) residue. In
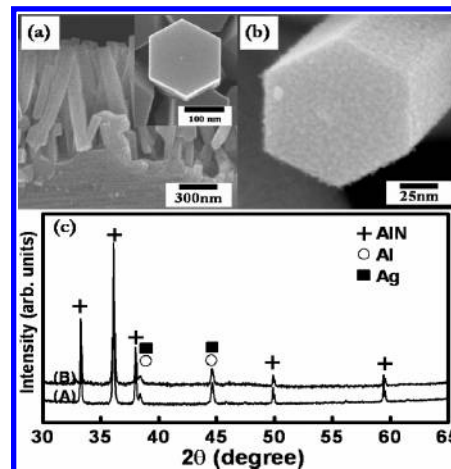

Figure 1. (a) Cross section and top view (inset) SEM image of quasi-aligned AlN nanorods. (b) Top view SEM image of Ag-coated AlN nanorod. (c) X-ray diffraction spectrum of as-grown and Ag-coated AlN nanorod, clearly showing a preferred orientation along [0002] (2θ = 36.04°).

addition to the XRD spectrum, the selected area electron diffraction (SAED) pattern (top inset, Figure 2a) and electron energy loss spectroscopy (EELS) (bottom inset, Figure 2a), carried out during transmission electron microscopy (TEM) measurements, conclusively prove that they are AlN in composition, having hexagonal symmetry. Figure 2a shows a TEM image of an Ag-coated AlN nanorod. Figure 2b shows the lattice image of the as-grown AlN nanorods with $d_{(0002)} = 0.252$ nm, matching that of h-AlN. The growth direction of the single-crystalline h-AlN nanorods was evidently [0002]. However, the role of the gold catalyst, buried within the Al seed crystal at the bottom of the rods, is not clearly understood.[9] We believe that it plays some part in controlling the morphology of the nanostructures.[9]

Having discussed the structure of these AlN nanorods, we now proceed to use them as templates for nanocrystalline Ag (nc-Ag) generation. SERS has been observed mostly on metal colloids prepared by wet chemistry,[10] which are often more efficient than the roughened silver electrodes[7] used conventionally. The problem with colloids, however, is their instability resulting from agglomeration. But, very importantly, clean-room-compatible plasma processes are always preferred over wet chemical means to incorporate the metal nanocrystals in a sensing device. Noble metals, such as Ag, that demonstrate the best SERS do form rough island-like films when deposited on silicon. The SERS activity of the metal is enhanced in the nanophase when a high packing density[11] is attained. Use of a wide band gap template, such as AlN, for the nanoparticle support is essential to eliminate any background luminescence effect from the support and accentuate the Raman

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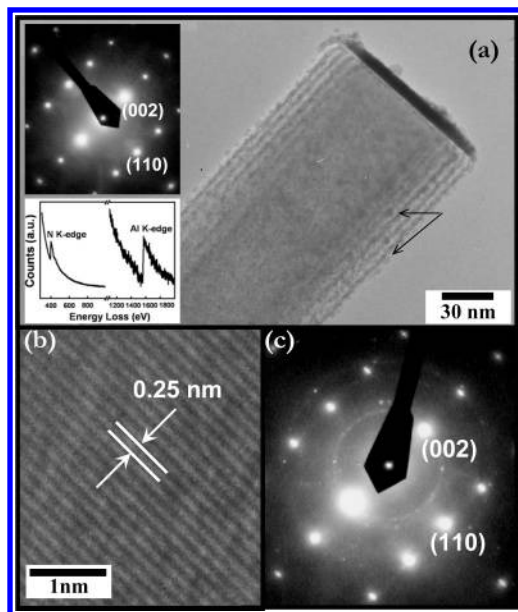# National Taiwan University.

Figure 2. (a) TEM image of a single Ag-coated AlN nanorod (the arrows showing the nc-Ag); top and bottom insets show the SAED pattern and the electron energy loss spectroscopy (EELS) spectrum of the as-grown AlN nanorod, respectively. (b) HRTEM image of the as-grown AlN nanorod lattice. (c) SAED pattern of the Ag-coated AlN nanorod.

signals. AlN, being chemically inert and immiscible with Ag, will also preserve the purity and integrity of the nc-Ag and can be utilized in fabricating stable and reliable plasma-engineered sensing devices.

The h-AlN nanorods provide a surface with suitable interface energy and lattice mismatch that promotes the generation of nc-Ag, instead of a thin film, under an incident flux of Ag vapors in a sputtering chamber with specified deposition parameters. Argon ion beam sputtering[12] of a Ag target for 10 min at room temperature and 5×10^{-4} Torr pressure, used in this case, produced a single coat of nc-Ag on the entire surface of the h-AlN nanorods. The sizes of the nc-Ag are mostly ~5 nm in diameter but not exceeding 10 nm, having an extremely high packing density such that they touch each other (Figure 1b). Note that the packing density of the nc-Ag, per unit probe volume, is further enhanced due to the rough nanostructured template compared to a flat template surface. Figure 2c shows the SAED pattern of the AlN nanorods with a postsynthesis coating of sputtered Ag. Clear and sharp diffraction spots, which are signatures of h-AlN, were observed in the SAED pattern, along with sharp ring patterns arising from nc-Ag (Figure 2c). The sharp ring features present in the SAED pattern (Figure 2c), but absent in Figure 2a (top inset), confirm the presence of nc-Ag in the Ag-coated samples. However, crystalline Ag cannot be detected unambiguously from the XRD spectrum of the Ag-coated h-AlN nanorods shown in Figure 1c (spectrum B), mainly due to a small cross section of the nc-Ag to the incident X-rays and the close proximity of the Ag (JCPDS file no. 03-0921) and unreacted Al signals. The Raman spectrum (Renishaw/UK, 2000 series Micro Raman spectrometer) of the as-grown h-AlN nanorods[6] excited by a 532 nm laser is shown in Figure 3a. Measured quantities (2−5 μL) of micromolar solutions of Rhodamine 6G (R6G) in methanol, when dropped on these as-grown h-AlN nanorods, show only a broad and strong fluorescence (Figure 3b) characteristic of R6G. The nc-Ag-coated h-AlN nanorod surface demonstrates SERS of 10^{-6} M R6G solution. The generally fluorescent R6G molecule
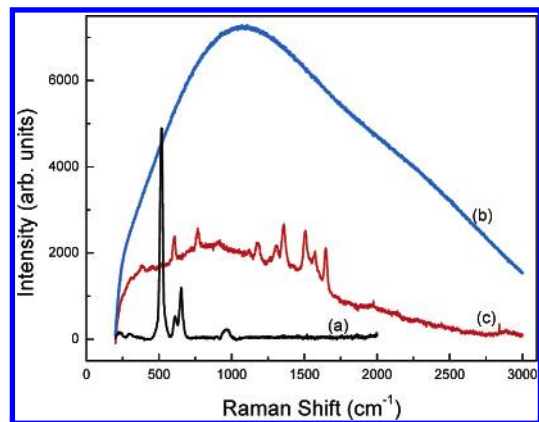

Figure 3. Raman spectrum of (a) the as-grown AlN nanorods and (b) the as-grown AlN nanorods with R6G, and (c) SERS spectrum of Ag-coated AlN nanorods with R6G.

has its fluorescence quenched when adsorbed on the nc-Ag present on the h-AlN nanorod template, and the Raman signals are promoted (Figure 3c). Assuming 100% adsorption of the R6G molecules on the nc-Ag, a minimum enhancement in the range of ~2×10^6 was calculated[13] for the Raman cross section.

In conclusion, we have demonstrated the synthesis of quasi-aligned h-AlN nanorods from pure Al powders heated to 1200 °C in the presence of ammonia. Ion-beam-sputtered silver self-assembles as nanocrystals on these h-AlN nanorods and readily exhibits surface-enhanced Raman scattering. Minimum SERS cross section enhancement factors around 2×10^6 have been obtained.

Supporting Information Available: SEM of the as-grown aluminum nitride nanorods and high-resolution TEM of the nanocrystalline silver on the AlN nanorod. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Davydov, V. Y.; Klochikhin, A. A.; Emtsev, V. V.; Ivanov, S. V.; Vekshin, V. V.; Bechstedt, F.; Furthmuller, J.; Harima, H.; Mudryi, A. V.; Hashimoto, A.; Yamamoto, A.; Aderhold, J.; Graul, J.; Haller, E. E. *Phys. Stat. Sol.* **2002**, *B 230*, R4.
(2) *Properties Processing and Applications of Gallium Nitride and Related Semiconductors*; Edgar, J. H., Strite, S., Akasaki, I., Amano, H., Wetzel, C., Eds.; INSPEC: London, 1999.
(3) Tondare, V. N.; Balasunbramaniam, S. V.; Shende, S. V.; Joag, D. S.; Godbole, V. P.; Bhoraskar, S. V.; Bhadbhade, M. *Appl. Phys. Lett.* **2002**, *80*, 4813.
(4) Wu, Q.; Hu, Z.; Wang, X.; Lu, Y.; Chen, X.; Hua, X.; Chen, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10176.
(5) Wu, Q.; Hu, Z.; Wang, X.; Lu, Y.; Huo, K.; Deng, S.; Xu, N.; Shen, B.; Zhang, R.; Chen, Y. *J. Mater. Chem.* **2003**, *13*, 2024.
(6) Wu, Q.; Hu, Z.; Wang, X.; Chen, Y.; Lu, Y. *J. Phys. Chem.* **2003**, *B107*, 9726.
(7) Fleishmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163.
(8) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102.
(9) Shi, S. C.; Chen, C. F.; Chattopadhyay, S.; Lan, Z. H.; Chen, K. H.; Chen, L. C. *Adv. Func. Mater.*, in press.
(10) Hildebrandt, P.; Stockburger, M. *J. Phys. Chem.* **1984**, *88*, 5935.
(11) Garcia-Vidal, F. J.; Pendry, J. B. *Phys. Rev. Lett.* **1996**, *77*, 1163.
(12) Wu, J. J.; Lu, T. R.; Wu, C. T.; Wang, T. Y.; Chen, L. C.; Chen, K. H.; Kuo, C. T.; Chen, T. M.; Yu, Y. C.; Wang, C. W.; Lin, E. K. *Diam. Relat. Mater.* **1999**, *8*, 605.
(13) Nikoobakht, B.; Wang, J.; El-Sayed, M. A. *Chem. Phys. Lett.* **2002**, *366*, 17.

JA042954L