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Mechanism of nanoblister formation in Ga^+ self-ion implanted GaN nanowires

S. Dhara,[a] A. Datta,[b] C. T. Wu, K. H. Chen,[c] and Y. L. Wang
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

S. Muto and T. Tanabe
Department of Nuclear Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

C. H. Shen, C. W. Hsu, and L. C. Chen
Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

T. Maruyama
The Wakasawan Energy Research Center, 64-52-1, Hase, Tsuruga 914-0192, Japan

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The formation of voids and bubbles during ion implantation is an important area of material research. Void and bubble formation can result in swelling and embrittlement of metallic or semiconducting materials, and increase catalytic effects in the nanopores of the bubble. Here, we report the observation of metallic nanoblister formation in GaN nanowires under self-ion implantation using a Ga^+ focused ion beam. The mechanism of the blister formation was resolved using high-resolution transmission electron microscopy equipped with electron energy loss spectroscopy and plasmon imaging. © *2005 American Institute of Physics.*
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The study of the interaction of energetic ions with materials has both fundamental and technological implications in diverse research areas. An important aspect of this field is the effect of high dose implantation on the structure of the materials. For example, the formation of voids and bubbles leading to increased volume is a consequence of: (1) displacement damage[1] and injection of inert gases;[2] or (2) disintegration and simultaneous accumulation of gaseous components of the target as a result of energetic ion–target interaction process.[3] Understanding the void or bubble formation and the resulting swelling and embrittlement is important in improving semiconductor technology. For example, recent bubble formation in a Cu matrix found applications in catalysis.[4] So far, the agglomeration of voids or bubbles is understood as the prime reason for the formation of large-scale volume swelling or blisters in metals or alloys.[5] Manifestation of the voids or bubbles in volume swelling seem to have similar influences in both elemental and compound semiconductors.[6–9] The excess volume swelling in self-ion implanted Si is reported to originate mainly from the vacancy clusters (nanovoids) present in the amorphous layer.[6] In compound semiconductors, both voids[7,8] and bubbles[3,9] are reported. This is a common feature in two-dimensional films and three-dimensional bulk systems, where the defect mobility is less pronounced relative to that in one-dimensional (1D) nanowire (NW) system. For subsurface implantation profile, e.g., as in the case of low energy ion implantation, surface deformation in the form of blistering was reduced or eliminated.[5] The reduction in blister formation was attributed to the enhancement of the mobility of the gaseous species due to the existence of the gas-saturated layer extending to the surface to provide a pathway for release and prevent the buildup of gaseous species to the critical concentration required for blistering. The present study is related to the observation of metallic nanoblister formation in self (Ga^+)-ion implanted GaN NWs.

Randomly oriented GaN NWs were formed by chemical vapor deposition technique using molten gallium as source and 10 sccm NH_3 as reactant gas. Thin film Au (~5 nm) is used as catalyst in the vapor–liquid–solid growth mechanism of wurtzite GaN NWs. Focused ion beam (FIB) was raster scanned at room temperature over an area of 400×400 μm with a beam current of ~1.3 nA corresponding to an ion flux of $\sim5\times10^{16}$ ions m^{-2} s^{-1} [$\sim15.6\times10^{-3}$ displacement per atom (dpa) s^{-1}]. This flux is comparable to the reported[3,9] value for irradiation studies in epitaxial (epi-) GaN film. Irradiation fluences of 1×10^{20} and 2×10^{20} m^{-2} corresponding to a maximum damage of ~62 dpa have been used in the present study. Calculations by Monte Carlo based SRIM code[10] shows that the 50 keV Ga^+ in GaN is a nuclear energy loss (~2 keV nm^{-1}) dominated process. Details of the growth of GaN nanowires and sample preparation using FIB is published elsewhere.[11]

Figure 1 shows the typical field emission scanning electron microscopic (Jeol-JSM-6700F) images of the nanoblisters formed by 50 keV Ga^+ self-ion implantation on GaN NWs at a fluence of 2×10^{20} m^{-2}. Nanoblisters of ~50–100 nm diameter is shown along with a large nanoblister in the inset (Fig. 1).

A high resolution transmission electron microscope (HRTEM) image [Fig. 2(a)] with a 1 MeV electron source (Hitachi H-1250ST) was used for the structural study of the blister region. Lattice imaging in Fig. 2(a) shows crystalline

[a]On leave from Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam-603102, India; electronic mail: dhara@igcar.ernet.in
[b]Now at Netaji Nagar Day College, 170/436 N.S.C Bose Road, Kolkata-700092, India.
[c]Author to whom correspondence should be addressed; electronic mail: chenkh@po.iams.sinica.edu.tw

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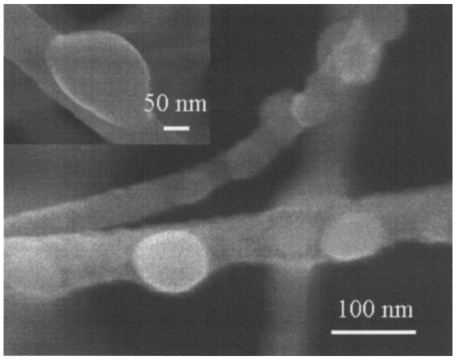

FIG. 1. FESEM images of the nanoblisters formed at 50 keV Ga^+ implantation on GaN nanowires with a fluence of 2×10^{20} ions m^{-2}. Inset shows a large nanoblister of diameter ~200 nm.

lattice corresponding to Ga in the blister and GaN in the NW region. Meanwhile, Fast Fourier transform (FFT) power spectrum as shown in Fig. 2(b) was calculated for the corresponding lattice images. This is to avoid the common problem of Ga melting (~302.8 K) during the SAED probing, which we have encountered during the transmission electron microscope (TEM) experiment. The zone axes in Fig. 2(b) correspond to [01−1] and [110] for α-Ga and wurtzite-GaN phases, respectively.

The pressure (P) inside the blister (radius, $R\sim40$ nm) is calculated[12] using $P=2\gamma/R+\mu b/R$ [surface energy (γ) of crystalline GaN 1.93 N m^{-1} (Ref. 13); shear modulus (μ) of wurtzite GaN 122.5 GPa;[14] and Burger vector (b) of GaN 0.8364 nm[15]] is about 3.0 GPa. At this pressure α-Ga phase is stable at room temperature.[16] The broadened Bragg spots corresponding to GaN lattice [Fig. 2(b)] may arise from the disordering and mosaic (small domains slightly misaligned to each other) nature of the crystalline GaN occurred upon irradiation. These defects may be correlated mainly to the large scale vacancies of Ga disintegrating from the lattice and partially contributing to the formation of nanoblisters. The contribution of Ga from the ion source falling in the base area of the blistered region is calculated to be ~4.0 nm only. The major Ga contribution to the blister is from the adjacent lattice which shows disorder [Fig. 2(a)] owing to probable Ga vacancy related defects. Radiation enhanced diffusion (RED) of either Ga^+ or lattice disintegrated Ga from sufficiently large distance in the NW and contributing to the blister also cannot be ruled out in the heavy ion implantation process. However, a small volume swelling is reported in electron-irradiated compound semiconductor, namely SiC, owing to the displacement of lighter element (C) and simultaneous agglomeration of Si either in the interstitial or antisite defect sites.[17] A dpa rate of $\sim4\times10^{-3}$ dpa s^{-1} was used for the study at room temperature. However, a large scale formation of blisters with the agglomeration of heavy elements is not addressed, particularly in compound semiconductors.

Formation of bubbles in heavy ion implanted epi-GaN film is reported to originate from disintegration and subsequent accumulation of gaseous nitrogen.[3,9] Formation of craters (blisters) was reported at a fluence of 3.5×10^{20} ions m^{-2} (~88 dpa) with 2 MeV Au^+ implantation in epi-GaN at 77 K using similar ion flux of $\sim5\times10^{16}$ ions m^{-2} s^{-1} $(\sim12.6\times10^{-3}$ dpa $s^{-1})$.[9] However, they failed to get any evidence of Ga precipitation in their process. In the present letter, we observed formation of nanoblisters containing α-Ga (Fig. 2) as the major constituent and the dpa value for the damage production was not very different from that found for nitrogen gas accumulated conventional blisters in the same material of GaN. Then question may be raised, as what is the reason for this anomalous behavior in the present study.

In order to resolve the anomaly, we made our observations (Fig. 3) in the sample irradiated at next lower fluence of 1×10^{20} ions m^{-2}. HRTEM [JEM3000F with Gatan Imaging Filter (GIF)] image showed small swelling within void like region lying near to surface [Fig. 3(a)]. We could not exactly determine the chemical nature of the constituent in the void like region. Thickness distribution of the NW is shown from the GIF image [Fig. 3(b)]. Plasmon imaging shows that Ga is segregated around and just below the void like region [Figs. 3(c) and 3(d)]. The plasmon imaging was done by selecting a particular energy corresponding to the spectrum feature [Fig. 3(f)] using an energy slit on the spectrum dispersion plane and obtaining the projected distribution of the particular phase or element as the bright region in the image. Nitrogen elemental imaging [Fig. 3(e)] also showed that the nitrogen is deficient around the surface of the wire. Appearance of a peak at 13.6 eV in the electron energy loss spectroscopy (EELS) [Fig. 3(f)] confirmed the depletion of N and accumulation of Ga around the void like region.[18] The broadening of the plasmon peak at 19.6 eV indicated severe damage of the GaN phase in that region.[18] Nitrogen might have accumulated initially in the void like region but escaped at a later stage owing to its large mobility near to the surface of

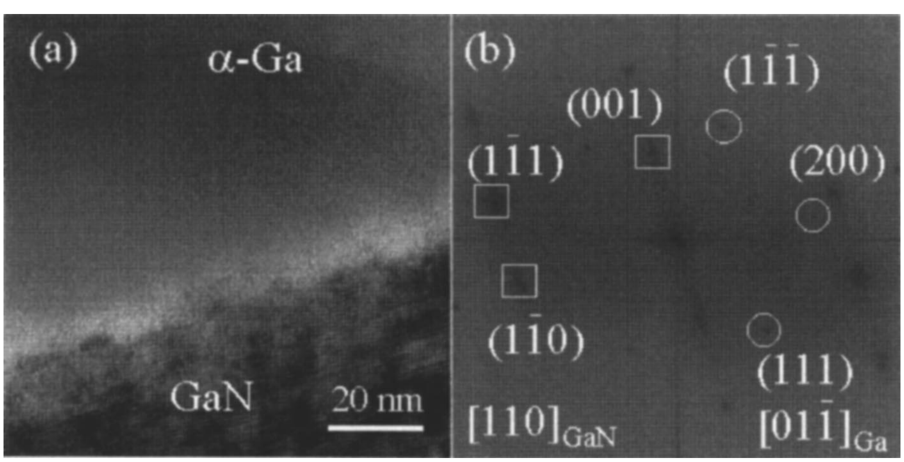

FIG. 2. HRTEM imaging with 1 MV electron source. (a) Lattice imaging of nanoblisters (top) formed at 50 keV Ga^+ implantation on GaN nanowires with a fluence of 2×10^{20} ions m^{-2} in the α-Ga phase and nanowire (underneath) wurtzite–GaN phase. (b) Calculated FFT power spectrum corresponding to the lattice images. The zone axes correspond to [01−1] and [110] for α-Ga and GaN phase, respectively.

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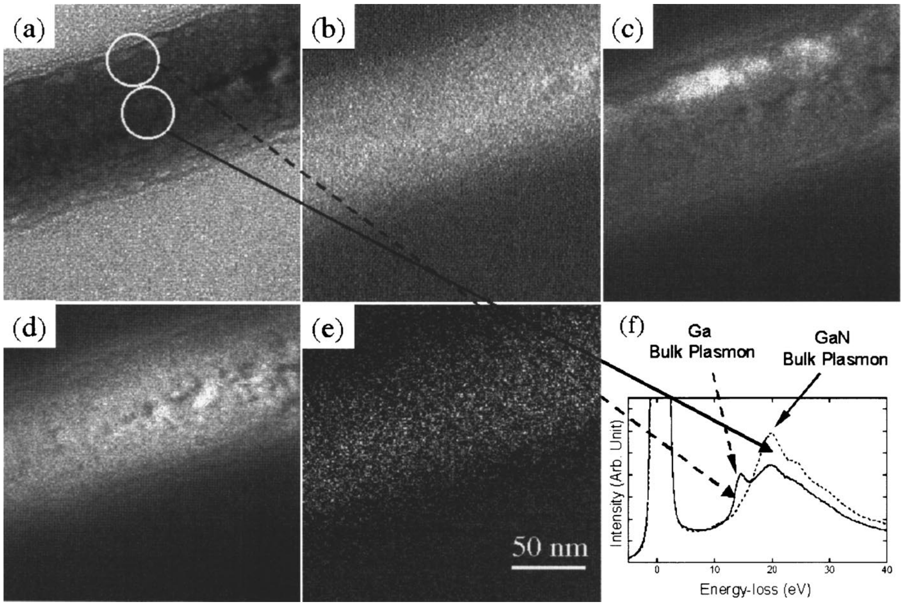

FIG. 3. Energy filtered electron microscopic images and EELS study of the void-like structure formed at 50 keV Ga^+ implantation on GaN nanowires with a fluence of 1×10^{20} ions m^{-2}. (a) HRTEM image; (b) energy filtered image for thickness distribution; (c) Ga plasmon image (at 15 eV, slit 3 eV); (d) GaN plasmon image (at 20 eV, slit 3 eV); (e) elemental nitrogen image; and (f) plasmon loss spectra corresponding to void-like region and nanowire region as indicated.

the 1D NWs. Appearance of the bubble structures close to the surface with low energy FIB irradiation and enhanced defect mobility in 1D system might have prevented further growth of conventional blisters with underlying bubble structure, as observed for the heavy ion implanted epi-GaN at high energy with defect structure lying at depth.[9] The reduction of blistering in bulk materials was also explained in terms of the gas-saturated layer extending to the surface to provide a pathway for release, which prevented the build up of gaseous species to the critical concentration required for blistering.[5]

It is worth mentioning here that Ga is a metallic molecular crystal with Ga_2-dimer as the building block for the face-centered-cubic orthorhombic α-Ga phase.[19] Moreover, Ga–Ga distance in GaN lattice is the same as the metallic Ga owing to the small radius of the N atom.[20] Therefore, Ga atoms around nitrogen vacancies (V_N's) form strong metallic bond during the disintegration process. Large energy deposition during the 50 keV self-ion (Ga^+) implantation in GaN nanowire also favors the formation of V_N's, as the formation energy of single V_N is only 4 eV in GaN.[20] Consequently, the nucleation of α-Ga phase via Ga_2 dimers is quite likely during the chemically clean self-ion implantation process. A large amount of precipitate forming the blister, as reported in the present study, can be realized only at high fluences when sufficient accumulation of Ga takes place. In the RED process of heavy ion implantation, Ga from sufficiently large distance may also contribute to the accumulation at high fluences.

In conclusion, Ga blisters were formed by Ga^+ self-ion implantation in GaN nanowires. Disintegration and accumulation of lattice atoms were found to be the dominant mechanism for the formation of metallic α-Ga nanoblisters. Shallow implantation with low energy FIB and enhanced defect mobility in 1-D system might have prohibited the formation of nitrogen blisters as observed for the heavy ion implanted epi-GaN at high energy with defect structure lying at depth.

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