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Effect of BN coatings on oxidation resistance and field emission of SiC nanowires

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We compare the effects of BN coatings on antioxidation ability and field emission properties of SiC nanowires. Under oxidizing condition, SiC nanowires without BN coatings are cracked into nanoparticles or almost fully converted into SiO₂ nanowires at the temperature above 800 K, depending on the crystallization degree of SiC nanowires. The BN coatings effectively improve the antioxidation ability of SiC nanowires due to the excellent chemical stability of BN at high temperature. At a temperature higher than 1273 K, the coated SiC nanowires still exhibit strong oxidation resistance. For the effect on electron emission, the BN coatings also reduce the turn-on field of SiC nanowires from larger than 10 V/ μ m to lower than 6 V/ μ m. The explanation for the improvement of field emission characteristics has been presented. © 2003 American Institute of *Physics*. [DOI: 10.1063/1.1595721]

It is well-known that refractory bulk SiC exhibits an excellent oxidation resistance at high temperature, because silica films formed on SiC serve as protecting against further oxidation.¹⁻³ The mechanism of the passive SiC oxidation is correlated with the reaction of $2SiC+3O_2 \leftrightarrow 2SiO_2+2CO$. The oxidation rate depends on the diffusion of oxygen through the formed SiO₂ layer followed by the reaction of SiC at the SiC-SiO₂ interface. The formed SiO₂ layer is considerably dense above 800 °C for bulk materials, and the oxidation basically follows a quadratic rate law.⁴ However, the investigation⁵ of the oxidation behavior of SiC fiber reinforced SiC matrix indicates that one-dimensional SiC exhibits strong oxidization with the rate constant of one order of magnitude higher than that of two-dimensional SiC matrix, due to the higher porosity, the larger specific surface, and the higher fraction of unprotected SiC fibers. Therefore, for downing to a scale of nanometer dimension, SiC nanowires are even more fragile to oxidation. In fact, the extent of the oxidation interaction between some metallic or semiconducting one-dimensional nanomaterials and oxidizing conditions is an important parameter in practically using them in the field of nanoelectronics and nanomechanics. However, few studies have been paid to the chemistry and physics degradation to date.6,7

The oxidation degradation can be weakened by coating nanomaterials with some chemically stable materials.^{8–10} Considering that BN has unique chemical and physical properties such as low density, high melting point, and chemical inertness, recently we have successfully coated SiC nanowires with uniform BN layers.¹¹ It is also worthy of note that this coating should have a strong influence on the electronic properties of SiC nanowires, for example, in the application of field emission. It has been reported that SiC nanowires (nanorods) exhibit good field emission properties in emission stability, but usually have a relatively high turn-on field typically higher than 10 V/ μ m.^{12,13} Theoretical investigations in-

dicate that BN coated one-dimensional materials are a very attractive system for reducing the applied field in cold electronic emission application.¹⁴ Therefore, the BN coated SiC nanowires should also be valuable for studying the mechanism of the promoting emission.

In this letter, we comparatively study the chemical stability and field emission of the SiC nanowires with or without BN coating. It is demonstrated that BN coating is effective in improving the antioxidation ability and the field emission characteristics of SiC nanowires.

SiC nanowires without BN coatings used in this study were synthesized by a shape memory synthesis process previously reported,¹⁵ using a reaction between SiO gas and carbon nanotubes. Two kinds of nanowires were chosen to investigate their oxidations: curved polycrystalline SiC nanowires [Fig. 1(a)] and highly crystallized straight SiC nanowires [Fig. 1(b)]. The former was synthesized at 1400 °C and kept the shape of the starting carbon nanotubes due to the carbon nanotubes space-confined effect; the latter was further crystallized at 1600 °C and its morphology was dominated by oriented single crystal growth mechanism. The



FIG. 1. The TEM image of the investigated nanowires: (a) curved polycrystalline SiC nanowires; (b) straight single-crystal SiC nanowires; (c) BN uniformly coated SiC nanowires with a great amount of stacking faults and microtwins, and (d) its high-resolution TEM image. The corresponding selected area electron diffraction patterns from a single nanowires were shown in (a), (b), and (c), respectively.

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FIG. 2. DTA-TG curves of SiC nanowires and TEM images after oxidizing at 1273 K for 2 h for (a) and (b) polycrystalline SiC nanowires; (c) and (d) single-crystal SiC nanowires; (e) and (f) BN coated SiC nanowires.

selected area electron diffractions (SAED) shown in the insets clearly exhibit the crystalline structure. Transmission electron microcopy (TEM) examinations indicate that the some incompletely reacted carbon distributes disorderedly in the polycrystalline nanowires, while no remnant carbon can be detected from the single-crystal nanowires. Figure 1(c) shows a TEM image of SiC nanowires with uniform BN coatings, which were synthesized within the framework of a vapor-liquid-solid growth mechanism.¹⁶ SAED indicates that the inner SiC nanowires contains a great amount of stacking faults and microtwins, however, the coated BN with the thickness of 2–4 nm exhibits highly crystallized layers with the same interlayer distance as one of BN nanotubes [Fig. 1(d)].

The oxidation behavior of SiC nanowires was investigated by differential thermal (DTA) and thermogravimetric (TG) analyses. The measurements were conducted in air atmosphere using a Thermo plus DTA–TG-8120 apparatus. The scan rate of temperature is fixed as 5 °C/min for three samples. Figures 2(a), 2(c), and 2(e) show the DTA and TG curves of polycrystalline, single-crystal and BN uniformly coated SiC nanowires, respectively.

For oxidation of polycrystalline SiC nanowires, there is weight loss of $\sim 1\%$ from 520 to ~ 640 K accompanied with an exothermal process. This is considered to correspond to the oxidation of the free carbon according to the reaction C $+O_2 \leftrightarrow CO_2$.⁵ The sequent exothermal peak occurs from \sim 860 to \sim 1120 K with a considerable weight loss of \sim 20%, indicating an occurrence of constituent volatilization in oxidizing conditions. It has been reported that,^{5,17} when SiO₂ layer formation is suppressed, a volatilization process will take place according to the reaction SiC $+O_2 \leftrightarrow (SiO)_{gas} + CO$. Therefore, the observed weight loss for polycrystalline SiC nanowires indicates that the protective SiO₂ layer on SiC nanowires has not yet been formed. When the environmental temperature is higher than 1150 K, the SiC gradually forms SiO₂ with the occurrence of the reaction $2SiC+3O_2 \leftrightarrow 2SiO_2+2CO.^{5,18}$

The oxidation of single-crystal SiC nanowires exhibits the similar behavior as polycrystalline nanowires, except for the absence of the oxidation of carbon because highly crystallized SiC nanowires do not contain free carbon. From 200 to ~ 800 K, weight gradually increases which implies a slow oxidization of SiC nanowires. From 800 to ~ 1000 K, the apparent weight loss and exothermal process can be observed, indicating that the similar volatilization as polycrystalline system occurs due to the lack of formation of SiO₂ protective layer.

The volatilization process does not occur during the oxidation of SiC nanowires with the BN coatings. From 200 to ~1100 K, there is almost no weight loss, implying the oxidation of BN and SiC has not yet taken place. From ~1100 to ~1210 K, a ~2% weight increase, accompanied with an exothermal process, can be observed from the DTA–TG curves. This could be explained according to the slow oxidation reaction of $4BN+3O_2 \leftrightarrow 2B_2O_3+2N_2$.^{18,19} Considering that within this temperature range boron oxide tends to form a vitreous structure with high viscosity, the volatilization of boron oxide should be considerably slow.²⁰ Moreover, the formed boron oxide can dissolve in the SiC nanowires matrix to generate a stable silicon borate layer.⁵ Above ~1400 K, the protection of BN layer is destroyed, and the oxidation of SiC drastically occurs.

To further determine the oxidation consequence, TEM examinations were carried out for the three samples, which all were oxidized in air at 1273 K for 2 h. Polycrystalline SiC nanowires cracked into nanoparticles with the size of several tens of nanometers [Fig. 2(b)]. Energy dispersive spectroscopy (EDS) measurements indicate that the nanoparticles mainly consist of SiO₂. Single-crystal SiC nanowires kept the starting one-dimensional morphology, however, the SiC was almost fully converted to SiO₂ although we can also observe some fractured SiC nanoparticles that are buried deep within the nanowires [Fig. 2(d)]. However, BN coated SiC nanowires exhibit an excellent antioxidation behavior under the same oxidizing condition. Figure 2(f) shows the typical morphology after oxidation. The oxidation has no apparent influence on the morphology and chemical structure of the inner SiC nanowires, although the coating BN became a dense amorphous layer. EDS analyses indicate that the BN layer contains O and Si, implying the existence of silicon borate product.

The field emission I-V characteristics of the SiC nanowires with and without BN coatings were measured in a vacuum chamber at a pressure of 10^{-8} Torr. A hemispherical-shaped stainless-steel probe of 0.8 mm in diameter (2R) was use as the anode. The anode was positioned by a linear-motion step controller. A voltage up to 1100 V was applied to the probe to collect emitted electrons from the ground cathode samples. The separation (Z) between anode and sample holder was fixed at 80 μ m for all experiments. The effective emission area (A) used to evaluate the current density and hopping field, was approximately calculated²¹ by $A = 2\pi RZ(2^{1/n} - 1)$, where $n = d \ln I/d \ln V$. Selected replicate experiments were conducted to determine the reproducibility of the measurements. Although the maximum accessible emission currents slightly vary with the number of the repeated measurements and with the voltage sweep rate, the maximum error of currents was less than 5%. The field emission from the free-standing BN nanotubes without carbon or metals contaminations, synthesized by MgO-promoted cata-



FIG. 3. Field emission plots for single-crystal SiC nanowires, BN nanotubes and BN coated SiC nanowires. The insets show the corresponding FN plots.

lytic growth methods,²² was also measured under same condition as comparison.

The average turn-on field was used as a figure of merit to compare various samples, which is defined as the applied electric field needed to produce a current density of 0.01 mA/cm^2 . Although the lowest turn-on field of about 3 $V/\mu m$ has been reported for oriented SiC nanowires synthesized by reacting aligned carbon nanotubes with SiO to date,²³ the single-crystal SiC nanowires discussed here showed a high turn-on field at 13 V/ μ m. The turn-on field of pure BN nanotubes is also larger than 14 V/ μ m (Fig. 3). However, the pattern of field emission of BN-SiC nanowires clearly showed a low turn-on field at 6, and $\sim 20 \text{ V}/\mu\text{m}$ of threshold field providing 10 mA/cm² of current density, which is typically required for effectively exciting a phosphor pixel in flat display. The values are comparable with the turn-on and threshold fields of carbon nanotubes, demonstrating that BN-SiC one-dimensional composite system is a promising emitting material for applications in flat display, if considering its excellent oxidation-resistance properties.

In order to understand the effect of the BN coatings on field emission of SiC nanowires, the obtained I-V curves were further analyzed using the classical Fowler-Nordheim (FN) theory by taking into account variations of geometric (field enhancement factor β) and electronic (effective potential barrier height ϕ) properties, although the theory usually results in an underestimation of barrier height especially for wide-band semiconductors.²⁴ According to this theory, the slope of $\ln(I/V^2) - 1/V$ curve is given by $-6.44 \times 10^7 \phi^{3/2}/\beta$. The FN plots for the three investigated specimen were shown in the inset of Fig. 3. The straight line relationships between $\ln(I/V^2)$ and 1/V are followed extremely well when the applied field is higher 300 V, suggesting that a quantum mechanical tunneling process is responsible for the electron emissions for three samples. The values of $\beta/\phi^{2/3}$ are defined from the FN plots to be 10870, 12060, and 36100 for SiC, BN, and BN-SiC, respectively. It is difficult to determine the enhancement factor, especially for materials with various morphologies and orientation. In the present study, a empirical formula²⁵ was adopted to calculate β , β = $1/[r \ln(4Z/r)]$, where 2r is diameter of nanowires. The model gives the β value dependent on emitter diameter and anode-cathode separation. Then, the effective barrier heights estimated from the earlier models are in the range of 1.9-2.8 eV for single-crystal SiC nanowires, 1.5–4.7 eV for pure BN nanotubes, and 0.5–1.0 eV for BN coated SiC nanowires. The values mean that the effective potential height of SiC nanowires is reduced at least to 1/3 due to the BN coatings. It is thus conjectured that the reduced barrier heights are the key factors that account for the reduction in turn-on field of the BN–SiC nanowires.

We believe that the low effective potential height of BN–SiC composite system is correlated with the electron behavior near the interface between wide-band semiconductor BN and SiC one-dimensional structures. It has been demonstrated by Sugina *et al.*^{26,27} that the deposition of BN nanofilms on some semiconducting substrates is effective in reducing the effective barrier height of the substrates.

In summary, BN coatings effective improve the antioxidation ability and reduce the turn-on field of SiC nanowires. The excellent chemical stability of BN is responsible for the improvement of antioxidation. The low turn-on field is due to a decrease of the effective potential barrier height, which is considered to result from the existence of a defect-induced positive space charge.

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