Nanometer-Thick Crystalline Carbon Films Having a Spinel Structure Grown on ZnO Substrates: Implications for New Ceramic–Carbon Composition

Norihiro Shimoi*

Cite This: ACS Omega 2020, 5, 32334−32340

ABSTRACT: I developed a bottom-up process of crystal growth using a field emission (FE) electron beam without transfer of heat energy. In this study, highly crystalline single-walled carbon nanotubes were used as the FE electron source. Acetylene was irradiated with an electron beam of high-resolution energy emitted from the electron source. Then, zinc oxide (ZnO) was irradiated with the carbon-based ions dissociated from the acetylene and electron beam, which formed a nonequilibrium excitation reaction field. As a result, a crystalline carbon thin film with a spinel-like structure different from the structures of graphite and diamond was grown on the ZnO surface. It is considered that the carbon film can be formed on substrates with a periodic crystal structure, not only ZnO. I confirmed that a carbon film with a periodic crystal structure independent of the crystal structure of the underlying substrate was grown, which bridged with the substrate. Thus, I have established a technique of crystal bridging between a ceramic and carbon for the first time to the best of our knowledge.

INTRODUCTION

In the formation of materials, general chemical processes, including the bonding and dissociation of heteroelements, involve heating or heat-releasing treatment regardless of the presence of catalysts. We have studied a bottom-up process for fabricating materials using an electron beam to form a nonequilibrium excitation reaction field as a means of transferring reaction energy without the transfer of heat energy. The process of bonding metals and other hetero-nanomaterials using a reaction field has been reported.1−5 We aim to establish a reaction process for high-ordered structures in a bottom-up architecture that is completely independent of the heating process in order to fabricate novel composites of ceramics and carbon, and we have been studying the synthesis of highly functional composite materials.

A nonequilibrium excitation reaction field was found to be a reaction field in which ceramic nanoparticles can be induced and manipulated by a focused electron beam and ions whose acceleration energy was controlled at the keV level.4,5 A beam and ions have conventionally been used in research on lattice defects in materials and surface modification. In the irradiation space, studies of a bottom-up specific reaction for the development of various nano- and microstructures have been carried out.6,7 In this study, we developed a technique for controlling the atomic arrangement by crystal bridging between a ceramic (ZnO) and carbon to fabricate novel composite materials with a low-speed field emission (FE) electron beam8−11 as a nonequilibrium excitation reaction field.

The technique used to synthesize various composite materials significantly affects their properties.12−24 Materials based on the bonding between metals and ceramics include metal–ceramic composites,12−14 heat-insulating ceramic coatings,15−17 electron device materials,18−20 and catalysts.21−24 For these composite materials, the interface between heteroelements with greatly different chemical bonding states significantly affects their physical and chemical properties.25,26 It is necessary to analyze the atomic structure and chemical bonding state of heteroelements at the interface and clarify their correlation with their properties. In this study, we achieved crystal bridging between ZnO and carbon in a nonequilibrium excitation reaction field and succeeded in forming a thin layer in which the carbon film with a structure different from those of graphite,27,28 diamond,29,30 and diamond-like carbon (DLC)31,32 is formed near the interface between the ZnO and carbon. In this paper, we report the crystal structure, chemical bonding, and the electron...
state of the ZnO–C interface from the viewpoint of crystallography.

## RESULTS

The hc-SWCNTs used as the electron source can achieve stable and long time FE even in a low vacuum of 2–3 Pa for both active and inactive gases. Figure 1a shows the relationship between the partial pressure of acetylene (C\(_2\)H\(_2\)) before and after dissociation (fixed at 1.6 Pa before dissociation) and the timing of FE, which was obtained using a quadrupole mass spectrometer (QMS; Canon Anelva Corporation). The FE current shown in Figure 1a was determined from the FE current density (dose rate) and the decrease in the partial pressure of acetylene shown in Figure 1b. The result in Figure 1 revealed that acetylene is dissociated into carbon- or hydrocarbon-based ions at a voltage of 20–30 V and a current density (dose rate) of \(\geq70 \text{ nA/cm}^2\). Exploiting the dissociation of acetylene by the electron source and electron beam, we performed an experiment in which ZnO nanoparticles were irradiated with the electron beam and carbon-based ions. The ZnO nanoparticles used in this study were synthesized by a wet process. They were exposed to a nonequilibrium excitation reaction field under the exposure conditions shown in Table 1. Figure 2 shows ZnO composites obtained at an acceleration voltage \((V_a)\) of 500 V, detected as micrometer diameter agglomerates after exposure. The nanoparticles before exposure had almost spherical shapes and a diameter of 10–100 nm and are shown in the inset of Figure 2, which is a field emission scanning electron microscopy (FE-SEM, Hitachi High-Tech Corporation) image taken at an acceleration voltage of 20 kV.

The composite obtained after exposure was embedded in resin and its surface was removed using a focused ion beam (FIB, FEI Company). As shown by the cross-sectional view in Figure 3a, small voids were observed inside the agglomerates. Macroskopically, elliptic ZnO particles, which were synthesized in this study exhibited selective crystal bridging along the c axis upon FE electron beam radiation as a nonequilibrium excitation reaction field,10,34 are concentrated and agglomerated. Figure 3b shows an enlarged view of the area within the white circle in Figure 3a. The area in the red circle in Figure 3b was further enlarged to analyze the composition distribution at the interface between the ZnO and the carbon film by point measurement using energy-dispersive X-ray spectroscopy (EDX, Hitachi High-Tech Corporation). Figure 3c shows a scanning transmission electron microscopy (STEM, Hitachi High-Tech Corporation) image of the same area. To analyze elements, spot tests were performed for zinc, oxygen, and carbon along the white arrow in the figure. Figure 3d shows the composition distribution of zinc, oxygen, and carbon obtained by EDX. It confirms that a film mainly composed of carbon was formed on the ZnO surface between the elliptic ZnO nanoparticles.

X-ray diffraction (XRD, Rigaku Corporation) crystallography was carried out to examine the exposed samples. The XRD pattern of a carbon thin film formed on a (100)-oriented Si substrate by the irradiation of carbon ions dissociated from acetylene by the electron beam was also obtained for reference. For the ZnO–C composite film, the XRD patterns are shown in Figure 4 for acceleration voltages \((V_a)\) of 100 and 500 V. The results indicate that the carbon films formed in this study have a structure different from that of graphite. The crystal structure (diffraction peak) of the carbon film formed on the Si substrate, shown as a reference, also matches that of the ZnO–C composite film. This suggests that the dissociation of acetylene by the electron beam and the existence of carbon-based ions generated after dissociation contribute to the formation of the carbon film with a structure different from that of graphite. In particular, the significant difference in the crystal structure owing to the acceleration energy is noteworthy. The crystal structure of

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c04214)

**Figure 1.** (a) Relationship between the decrease in the partial pressure of acetylene owing to dissociation and the FE current, obtained using a QMS, and (b) the relationship between the FE current density and the decrease in the partial pressure of acetylene.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c04214)

**Figure 2.** SEM image of wet-synthesized ZnO nanoparticles irradiated with an electron beam and carbon ions (inset: ZnO nanoparticles before irradiation).

---

**Table 1. Conditions of Exposure to a Nonequilibrium Excitation Reaction Field**

| parameters | values |
|------------|--------|
| electron source, FE size | 15 \(\times\) 15 mm\(^2\) |
| FE voltage \((V_a)\) | 22.0 V |
| FE current density (dose rate) | 90 nA/cm\(^2\) \(\times\) \(10^{16}\) electrons/cm\(^2\) |
| acceleration voltage \((V_a)\) | 100 and 500 V |
| vacuum level | 1.6 Pa |

---

32335

https://dx.doi.org/10.1021/acsomega.0c04214

ACS Omega 2020, 5, 32334–32340
the carbon film was clearer for the reaction field with the higher acceleration voltage. The crystal structure of the carbon film formed on the Si substrate is different from that identified from the diffraction peaks of the reported silicon carbide (SiC). It is
considered that the carbon film obtained in this study has a unique crystal structure that does not depend on the crystal structure of the underlying substrate.

To examine the crystal structure of the interface between the ZnO and the carbon film in more detail, a high-resolution transmission electron microscopy (HRTEM, JEOL, Ltd.) image was obtained at an acceleration voltage of 300 kV (Figure 5a).

![Figure 5](https://example.com/figure5.png)

**Figure 5.** (a) HRTEM image of the interface between ZnO and carbon film near the ZnO surface, (b) the diffraction pattern of ZnO, (c) the FFT pattern of the diffraction image of the carbon film near the ZnO surface in the red circle in (a).

The measurement sample in Figure 5 was cut again to the piece shown in Figure 3 by a FIB for HRTEM. Figure 5a shows an HRTEM image of the interface between the ZnO and the carbon film. An ~20 nm-thick carbon film was formed on the ZnO surface, confirming a clear interface between the ZnO and the carbon film. Figure 5b shows the diffraction pattern of the ZnO. This pattern represents the arrangement of the ZnO in the direction of the c axis. As shown in Figure 5a,b, the ZnO layers along the c axis and the carbon film graphite layers are parallel, forming a clear interface. Moreover, another layer formed in the space of the carbon film corresponding to the gap between the ZnO layers, suggesting that atomic or molecular layers different from graphite layers were formed. Figure 5c shows the fast Fourier transform (FFT) pattern of the diffraction image at a position corresponding to the carbon film. The FFT pattern represents a diffraction image different from that in the ZnO region, meaning that the crystal structure of the carbon film is fundamentally different from that of the ZnO. Assuming that Figure 5b shows the crystal structure of the ZnO itself, the plane orientations of the diffraction pattern are shown in Figure 5c, indicating that a spinel-like crystal structure was formed. At a position on the carbon film far from the ZnO surface, a polycarbon-like carbon film formed, in which multiple graphite layers were laminated.

As mentioned above, we confirmed the existence of another layer on the carbon film formed near the ZnO surface and positioned in the interlayer gap; this layer exhibits a diffraction image corresponding to that of the ZnO. A continuous crystal structure different from that of graphite or diamond layers is considered to have been formed.

Figure 6 shows absorption spectra of carbon obtained by Fourier transform infrared (FTIR) spectroscopy (JASCO Corporation). The results for the ZnO–C composites formed by the irradiation of the electron beam and carbon-based ions at acceleration voltages of 100 and 500 V and for carbon films formed on Si and glass substrates for reference.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** FTIR spectra of ZnO–C composites and the carbon film grown on a Si substrate. For reference, an FTIR spectrum of the carbon film grown on a glass substrate is also shown.

For the ZnO–C composites and the carbon film on the Si substrate, carbon bonds corresponding to sp and sp^2 C and hydrocarbon-related bonds corresponding to sp and sp^3 CH were clearly observed. In particular, the higher the acceleration energy, the clearer the peaks are for sp and sp^2 C. These spectra are similar to those of DLCs. The crystal structure is a mixture of a graphite layer structure and a tetrahedral or diamond structure. Furthermore, the carbon film on the Si substrate has an electron bond state similar to that of the carbon film on the ZnO, and no peaks corresponding to carbon bonds were observed for the carbon film on the glass substrate. These results suggest that the crystal structure of the carbon film is independent of the dangling bonds and periodic crystal structure of the underlying substrate. Figure 7 shows X-ray photoelectron spectroscopy (XPS) spectra of the ZnO–C composite particles shown in Figure 2. The spectra correspond to the carbon bond and the oxygen bond (Figure 7a,b). It was found (1) that no peaks exist that correspond to the bonds of metals with carbon (carbides), (2) that a tetrahedral carbon bond state corresponding to a diamond structure with an electron state related to the sp^3 orbital exists, and (3) that most peaks correspond to the bonds of metals (Zn in this study) with oxygen. The peaks corresponding to CO and OH are considered to be due to the components generated by the dissociation of acetylene and those synthesized with the ZnO as well as carbon oxide on the composite surface.

### CONCLUSIONS

The analysis of our results revealed that carbon film is formed on a ZnO surface when ZnO is irradiated with carbon-based ions and an FE electron beam accelerated to 500 V to provide a nonequilibrium excitation reaction field. The low-energy FE electron beam is generated using hc-SWCNTs and dissociates acetylene during the process. In the carbon film, graphene-like thin film layers and graphene-like layers are laminated. The distance between the graphene-like thin film layers is considered to depend on the periodic crystal structure of the substrate on which the ZnO crystals are grown. Figure 8 shows a schematic of crystal bridging between the ceramic material ZnO and the carbon. The distance between graphene layers for stable graphite is approximately 0.33–0.35 nm, while the c axis interlayer distance of ZnO is 0.53 nm as shown in Figure 5a. The interlayer distance of ZnO is about 1.7 times that of graphite.
and it is impossible for each graphite interlayer to cross-link with ZnO in the same c axis direction. The carbon layer was found to be cross-linked with almost every c axis layer of ZnO, and the existence of a cross-linking network with the upper and lower carbon layers was necessary for the intermediate layer to be cross-linked. In addition, no heteroelements were intercalated into the graphite layer, and another carbon atomic layer was grown in the gap between the layers, that is, the thin film was composed of only pure carbon. Figure 8 shows an image of the crystal structure of the ZnO layer, which is based on the hybridization of sp² and sp³ orbitals revealed from Figures 6 and 7 and the spinel-like crystal pattern indicated by the FFT diffraction pattern in Figure 5.

In this study, we fabricated carbon thin films using ZnO and a reference Si substrate. In addition to the growth of such films on metals and semiconductors, it is expected that a periodic crystal structure of pure carbon that is different from those of graphite, diamond, and DLC can be fabricated by controlling the acceleration energy of the electron beam and carbon-based ions to achieve crystal bridging between ZnO and the carbon film, and we obtained a new composite comprising ZnO and carbon film. In the future, we expect to synthesize not only zinc oxide but also highly functional materials by fusing ceramics and carbon using a nonequilibrium reaction field, and we will attempt to synthesize ceramic—carbon composite materials with high electrical, physical, and chemical functionalities.

### EXPERIMENTAL METHODS

In this study, an FE electron beam was used to form a nonequilibrium excitation reaction field. Compared with thermal electron beams, the FE electron beam can achieve a narrower energy distribution in accordance with the principle of...
FE\textsuperscript{36} and can efficiently emit a large number of electrons with a large amount of electron irradiation (current) at a low voltage.\textsuperscript{37}

To emit electrons more efficiently at a lower driving voltage, we used highly crystalline single-walled carbon nanotubes (hc-SWCNTs) for the electron source. This is because hc-SWCNTs are expected to achieve stable FE and are suitable for arbitrarily controlling the amount of FE from pA to A.\textsuperscript{37} We added hc-SWCNTs to a conductive thin film to form a planar FE electron source and constructed a system for forming a nonequilibrium excitation reaction field. Figure 9a shows a schematic of the system. The planar electron source with added hc-SWCNTs was used as a cathode, and an electrode covered by hc-SWCNTs to a conductive thin film to form a planar FE electron source in low vacuum (1.0 Pa). FE was successfully controlled at the nA order at an applied voltage of <40 V.

**AUTHOR INFORMATION**

**Corresponding Author**

Norihiro Shimoi – Department of Electrical and Electronic Engineering, Tohoku Institute of Technology, Sendai 982-8577, Japan; e orcid.org/0000-0002-3787-3767; Phone: +81-22-305-3214; Email: n-shimoitohotech.ac.jp

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04214

**Notes**

The author declares no competing financial interest.

**REFERENCES**

(1) Alexander, B. H.; Balluffi, R. W. The mechanism of sintering of copper. Acta Metall. 1957, 5, 666–677.

(2) Ardell, A. J. The effect of volume fraction on particle coarsening: theoretical considerations. Influence de la fraction volumique sur le grossissement des particules: considerations theoriques. Der einfluss des volumenanteils an der Teilchenvergroesserung: theoretische Uberlegungen. Acta Metall. 1972, 20, 61.

(3) Bae, S. I.; Baik, S. Determination of Critical Concentrations of Silica and/or Calcia for Abnormal Grain-Growth in Alumina. J. Am. Ceram. Soc. 1993, 76, 1065–1067.

(4) Locke, B. R.; Shih, K.-Y. Review of the methods to form hydrogen peroxide in electrical discharge plasma with liquid water. Plasma Sources Sci. Technol. 2010, 20, No. 034006.

(5) David, S. A.; Babu, S. S.; Vitek, J. M. Welding: Solidification and microstructure. JOM 2003, 55, 14–20.

(6) Yilbas, B. S. Entropy analysis in an Au-Cr two-layer assembly during laser short pulse heating. Numer. Heat Transfer, Part A 2003, 43, 179–199.

(7) Edmondson, P. D.; Young, N. P.; Parish, C. M.; Moll, S.; Namavar, F.; Weber, W. J.; Zhang, Y. Ion-Beam-Induced Chemical Mixing at a Nanocrystalline CeO\textsubscript{2}-Si Interface. J. Am. Ceram. Soc. 2013, 96, 1666–1672.

(8) Fujimura, T.; Tanaka, S.-I. In-Situ High temperature X-ray diffraction study of Cu/Al\textsubscript{2}O\textsubscript{3} interface reactions. Acta Mater. 1998, 46, 3057–3061.

(9) Cheng, B.; Yu, X.; Liu, H.; Fang, M.; Zhang, L. Enhanced effect of electron-hole plasma emission in Dy, Li codoped ZnO nanostructures. J. Appl. Phys. 2009, 105, No. 014311.

(10) Shimoitoh, N.; Tanaka, S.-I. Nonthermal crystal bridging of ZnO nanoparticles by nonequilibrium excitation reaction of electrons and plasma without cross-linking agent on plastic substrate. J. Alloys Compd. 2011, 79, 676–683.

(11) Shimoitoh, N.; Tohji, K. Field-emission durability employing highly crystalline single-walled carbon nanotubes in a low vacuum with activated gas. J. Phys. D: Appl. Phys. 2019, 52, 505303.

(12) Iwamoto, C.; Tanaka, S.-i. Interface nanostructure of brazen silicon nitrid. J. Am. Ceram. Soc. 1998, 81, 363–368.

(13) Eustathopoulos, N. Dynamics of wetting in reactive metal ceramic systems. Acta Mater. 1998, 46, 2319–2327.

(14) Rado, C.; Drevet, B.; Eustathopoulos, N. The role of compund formation in reactive wetting: The Cu/SiC system. Acta Mater. 2000, 48, 4483–4491.

(15) Donald, I. W. Preparation, properties and chemistry of glass- and glass-ceramic-to-metal seals and coatings. J. Mater. Sci. 1993, 28, 2841–2886.

(16) Kobuto, T.; Miyaji, F.; Kim, H.-M.; Nakamura, T. Spontaneous formation of bonelikeapatite layer on chemically treated titanium metals. J. Am. Ceram. Soc. 1996, 79, 1127–1129.

(17) Kim, H.-M.; Miyaji, F.; Kobuto, T.; Nakamura, T. Effect of heat treatment on apatite-forming ability of Ti metal induced by alkali treatment. J. Mater. Sci. Mater. Med. 1997, 8, 341–347.

(18) Llorca, J.; Needlemann, A.; Suresh, S. An analysis of the effects of matrix void growth on deformation and ductility in metal ceramic composites. Acta Metall. 1991, 39, 2317–2335.

(19) Miotello, A.; Kelly, R.; Laidani, N. Chemical and compositional changes induced by ion implantation in SiC and resulting hydrogen permeation properties. Surf. Coat. Technol. 1996, 65, 45–56.

(20) Santos, M.; Filipe, E. C.; Michael, P. L.; Hung, J.; Wise, S. G.; Bilek, M. M. Mechanically Robust Plasma-Activated Interfaces Optimized for Vascular Stent Application. ACS Appl. Mater. Interfaces 2016, 8, 9635–9650.

(21) Jo, W.; Kim, D.-Y.; Hwang, N.-M. Effect of interface structure on the microstructural evolution of ceramics. J. Am. Ceram. Soc. 2006, 89, 2369–2380.

(22) Du, H.-B.; Li, Y.-L.; Zhou, F.-Q.; Su, D.; Hou, F. One-Step Fabrication of Ceramic and Carbon Nanotube (CNT) Composites by In S itu Growth of CNTs. J. Am. Ceram. Soc. 2010, 93, 1290–1296.

(23) Shimoitoh, N.; Tanaka, S.-I. Enhancement of electron field emission from carbon nanofiber bundles separately grown on Ni catalyst in Ni-Cr alloy. Carbon 2009, 47, 1258–1263.

(24) Yan, J.; Yu, J.; Ding, B. Mixed Ionic and Electronic Conductor for Li-Metal Anode Protection. Adv. Mater. 2018, 30, 1705105.

(25) Kruth, J.-P.; Levy, G.; Klocce, F.; Childs, T. H. C. Consolidation phenomena in laser and powder-bed based layered manufacturing. CIRP Ann. 2007, 56, 730–759.

(26) Hagman, P. J.; Finn, R. C.; Zubierta, J. Molecular manipulation of solid state structure: influences of organic components on vanadium oxide architectures. Solid State Sci. 2001, 3, 745–774.

(27) Geim, A. K.; Novoselov, K. S. The rise of graphene. Nat. Mater. 2007, 6, 183–191.

(28) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature 2009, 457, 706–710.

(29) Moulton, B.; Zaworotko, M. J. From molecules to crystal engineering: Supramolecular isomerism and polymorphism in network solids. Chem. Rev. 2001, 101, 1629–1658.

(30) Balandin, A. A. Thermal properties of graphene and nanostructured carbon materials. Nat. Mater. 2011, 10, 569–581.
(31) Kuznetsov, V. L.; Chuvilin, A. L.; Butenko, Y. V.; Mal’kov, I. Y.; Titov, V. M. Onion-like carbon from ultra-disperse diamond. *Chem. Phys. Lett.* **1994**, *222*, 343−348.

(32) Sengupta, R.; Bhattacharya, M.; Bandypadhyay, S.; Bhowmick, A. K. A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites. *Prog. Polym. Sci.* **2011**, *36*, 638−670.

(33) Meulenkamp, E. A Synthesis and growth of ZnO nanoparticles. *J. Phys. Chem. B* **1998**, *102*, 5566−5572.

(34) Vayssieres, L. Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions. *Adv. Mater.* **2003**, *15*, 464−466.

(35) Morkoç, H.; Strite, S.; Gao, G. B.; Lin, M. E.; Sverdlov, B.; Burns, M. Large-band-gap SiC, III-V nitride, and II-VI ZnSe-based semiconductor device technologies. *J. Appl. Phys.* **1994**, *76*, 1363−1398.

(36) Kimoto, K. Practical aspects of monochromators developed for transmission electron microscopy. *Microscopy* **2014**, *63*, 337−344.

(37) Shimoi, N.; Sato, Y.; Tohji, K. Highly Crystalline Single-walled Carbon Nanotube Field Emitters: Energy-loss-free High Current Output and Long Durability with High Power. *ACS Appl. Electron. Mater.* **2019**, *1*, 163−171.