

Spontaneous graphenization of amorphous carbon on clean surfaces of nanometer-sized nickel particles at room temperature



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ABSTRACT

We studied the structures of amorphous carbon (a-C) films deposited on nickel (Ni) nanoparticles with clean surfaces by transmission electron microscopy and Raman spectroscopy. The Ni nanoparticles were prepared on cleaved sodium chloride substrates by electron beam deposition at a base pressure of less than 3×10^{-7} Pa at 673 K, and subsequently the a-C film was deposited onto the nanoparticles at room temperature without exposure to air. The a-C around the Ni nanoparticles spontaneously formed a disordered graphitic structure without heat treatment. This contrasts markedly with the case in which Ni nanoparticles were exposed to air once, and no graphitic layer formed on the surfaces of the nanoparticles unless a heat treatment was performed. The present results suggest that clean surfaces of metal nanoparticles without exposure to air exhibit high catalytic activity and reduce the graphenization temperature of a-C.

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1. Introduction

Graphene, which is composed of a single atomic layer of graphite, has attracted a lot of interest owing to its extraordinary properties, such as high carrier mobility, thermal and electrical conductivity, and mechanical strength [1–5], which have led to many applications [6]. Graphene has been produced by various methods, such as mechanical exfoliation of graphite, chemical vapor deposition using catalytic transition metals, and annealing of silicon carbide [7–9]. A more recent approach to synthesizing graphene involves annealing a solid carbon source, such as a polymer film or an amorphous carbon (a-C) film, on a metal catalyst substrate [10–14]. The metal-catalyzed graphenization of a-C films can be used to produce large-area graphene and improve the quality of graphene, which furthers the development of graphene-based devices. The mechanism of the metal-catalyzed graphenization of a-C films reportedly involves the dissolution of carbon into the catalytic metal at temperatures above 873 K and the precipitation of carbon as graphene on the catalytic metal surface from the solid solution during cooling. Thus, it is expected that the initial state of the catalytic surfaces serving as a reaction field is very important for the formation of graphene. However, it seems that

previous studies on metal-catalyzed graphenization of a-C films have not paid much attention to the initial surface state of the catalytic metals, in particular, the cleanliness of the catalytic surfaces. In many studies for metal-catalyzed graphenization of a-C, nickel (Ni) substrates were used as catalysts [10–14]. Here, we used the clean surfaces of nanometer-sized Ni particles as the catalysts and studied the structure of as-deposited a-C films on these Ni nanoparticles by transmission electron microscopy (TEM) and Raman spectroscopy.

2. Experimental

Specimens were prepared by electron beam deposition using a 980-7401 four source E-type electron gun (CANON ANELVA CORPORATION) in an ultrahigh vacuum chamber with a base pressure of less than 3×10^{-7} Pa. Sodium chloride (NaCl) (001) surfaces cleaved in air were used as substrates. Pure Ni (99.99%, Kojundo Chemical Laboratory Co., Ltd.) and pure carbon rods (99.998%, Nippon Carbon Co., Ltd.) were used as evaporation sources. Ni was deposited onto the NaCl (001) substrates, which were maintained at 673 K during deposition. Subsequently, C was deposited onto Ni at room temperature, without exposing the specimens to air. The mean thicknesses of the deposited Ni and C layers were 0.8–1.0 nm and 10.0–15.0 nm, respectively. In order to examine the influence of the surface state, C was also deposited onto the Ni layer of NaCl (001) specimens that were exposed to air after Ni deposition. For

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the preparation of TEM and Raman spectroscopy samples, the NaCl substrates were dissolved in distilled water and the as-deposited films were picked up onto molybdenum TEM grids. The structures of the specimens were observed by high-resolution TEM and electron diffraction using a JEM-2010 transmission electron microscope (JEOL Ltd.). The microscope was operated at an acceleration voltage of 120 kV. Raman spectra for the specimens were measured with a Renishaw inVia Reflex Raman microscope using a 532-nm laser excitation at room temperature.

3. Results and discussion

Fig. 1(a) and (b) show a TEM image of the carbon film deposited onto Ni without exposing to air and its selected-area electron diffraction pattern, respectively. Ni is composed of isolated nanometer-sized particles. The electron diffraction pattern in Fig. 1(b) consists of a halo pattern and single-crystalline spots. The spots are assigned to fcc-Ni with [001] incidence. The lattice spacing of the Ni nanoparticles is slightly larger than that in bulk Ni, e.g., the spacing of (200) and (220) planes of the nanoparticles are 1.81 and 1.28 Å, which are 2.7% wider than that of bulk Ni (1.762 and 1.246 Å), respectively. The halo pattern comes from the amorphous carbon film. The orientation relationship of the Ni nanoparticles grown on NaCl (001) is $[100]_{\text{Ni}}//[100]_{\text{NaCl}}$, $(001)_{\text{Ni}}// (001)_{\text{NaCl}}$. Most of the Ni nanoparticles in Fig. 1(a) show a rectangular profile. The size distribution of the Ni nanoparticles is shown in Fig. 1(c), where the diagonal of the rectangular profile is used as the size of the nanoparticle. The average size of the nanoparticles and its standard deviation are estimated to be 5.7 and 0.8 nm,

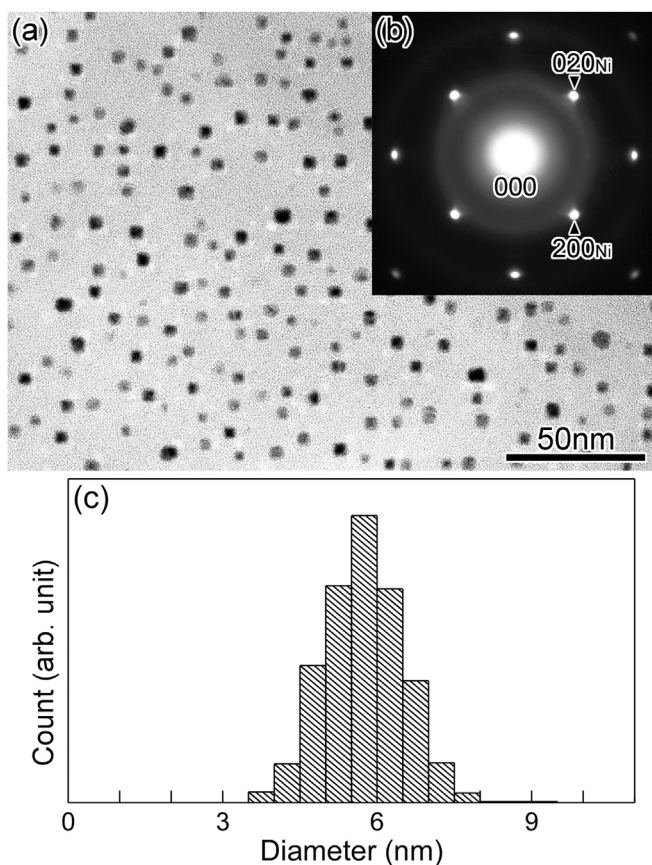


Fig. 1. (a) TEM image and (b) selected-area electron diffraction pattern of the a-C film deposited onto Ni nanoparticles without exposing the nanoparticles to air. (c) Size distribution of the Ni nanoparticles in (a).

respectively (Fig. 1(c)). Fig. 2(a) shows a high-resolution image of the specimen in Fig. 1. Note that disordered graphitic layers, similar in structure to carbon black [15], are already formed only around the surfaces of the Ni nanoparticles without annealing. The number of layers is more than four. The spacing of the layers indicated by the arrows in Fig. 2(a) is about 0.36 nm, which is 4.3% wider than that of graphite. Fig. 2(b) shows a Raman spectrum measured from the specimen in Fig. 1. The G peak and D peak appear at 1573 and 1377 cm^{-1} , respectively, which are different from the Raman spectrum for a-C [16]. This indicates that the as-deposited carbon film consists of a-C and disordered graphite, as seen on the surface of the Ni nanoparticles in Fig. 2(a) [17]. The present observations suggest that spontaneous graphenization of a-C on the clean surfaces of Ni nanoparticles occurs at room temperature.

In order to elucidate the influence of the surface state of Ni nanoparticles upon the formation of disordered graphitic layers, a-C films deposited on the Ni nanoparticles at room temperature after exposing the nanoparticles to air were examined. Fig. 3(a) and (b) show a TEM image of an a-C film deposited onto Ni nanoparticles after air exposure and the corresponding electron diffraction pattern, respectively. The average size of the Ni nanoparticles is about 6.6 nm. The faceted Ni nanoparticles are oriented in the same

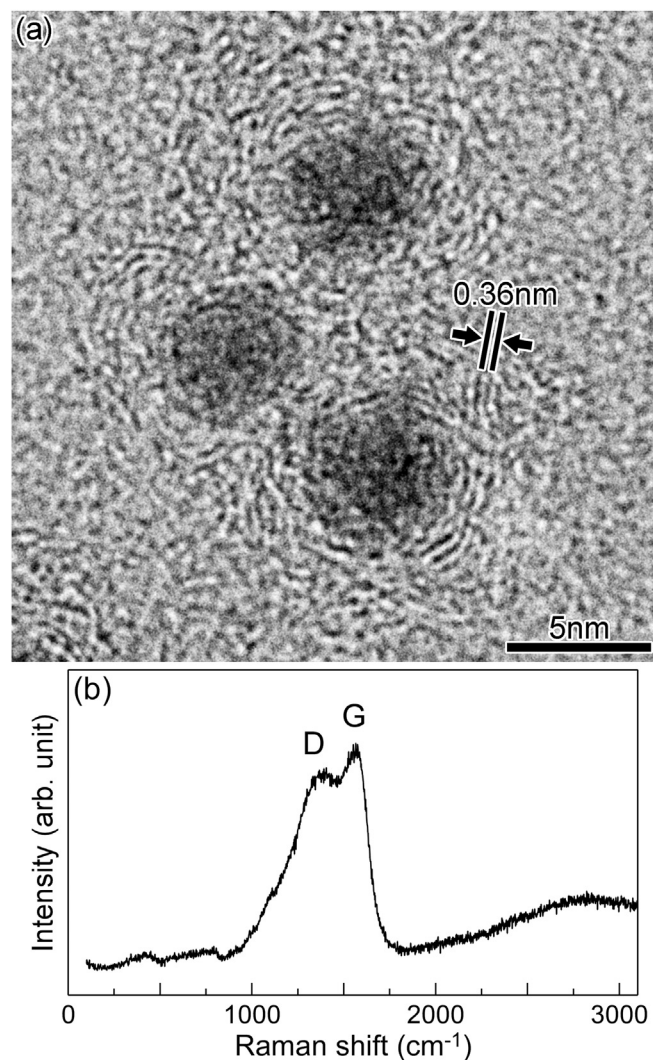


Fig. 2. (a) High-resolution image and (b) Raman spectrum for the specimen in Fig. 1. Disordered graphitic layers are formed only around the surface of the Ni nanoparticles at room temperature without annealing.

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