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LETTER

Effect of dynamic precursor gas pressure on growth behavior of amorphous Si–C–O nanorods by electron beam-induced deposition

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Electron beam-induced deposition (EBID) is a versatile maskless technology [1] to fabricate submicron- or nanometerscale structures from various elements in scanning electron microscope [2] as well as transmission electron microscope [3] and scanning transmission electron microscope [4]. During EBID, adsorbed precursor gas molecules on a substrate surface are irradiated and dissociated by an electron beam. This induces a chemical reaction that results in the deposition of non-volatile materials. If the electron beam is not moved relative to the substrate, a nanodot can be formed; electron beam scanning can produce nanorod within a suitable precursor gas pressure. Nanofabrication by using EBID is hence exceeding in terms of controlling the position and morphology of low dimensional functional nanostructures, e.g., carbon nanotube and ferromagnetic FePt alloy nanorods [5, 6]. It is very necessary to probe the effects of various deposition parameters on the target deposits, e.g., electron beam scan speed, precursor gas pressure, and deposition time, in order to fully develop and improve EBID serving as nanotechnology. No much importance, however, has been attached to *dynamic* precursor gas pressure in EBID, although it is generally known that the higher the precursor gas pressure is, the more the decomposed gas molecules are, and the larger the size of the deposits should be during EBID [7–9]. Undoubtedly, it will be the most direct route to know about the transport of precursor gas molecules by real-time monitoring (dynamic) precursor gas pressure, which helps to unravel the microscopic effect of gas pressure on the successive nanofabrication. In this paper, we will investigate the effects of dynamic precursor gas pressure and electron beam scan speed on the EBID process.

Electron beam-induced deposition experiment was carried out in a 30 kV field emission gun scanning electron microscope (JEOL JSM-7800UHV). The electron beam current was about 0.8 nA with a beam diameter of 4 nm. The irradiation position and time of electron beam were controlled by an external voltage input to the beam deflectors using a computer with digital–analog converters. Tetraethoxy-silane $SiOC_2H_5$ was used as a precursor. A gas introduction system consists of a nozzle (its tip was about 1 mm away from the electron beam position, as shown in Fig. 1), gas pipeline, variable leak valve, and gas source reservoirs. The base gas pressure in the specimen chamber was 2×10^{-6} Pa and the maximum allowable gas pressure is 2×10^{-4} Pa. A holey carbon film was used as substrates.

A 300 kV JEM-3000F field-emission gun transmission electron microscope, attached with a post-column Gatan imaging filter and a 1 k × 1 k Ultrascan CCD camera, was employed to characterize the deposits by a high-resolution transmission electron microscopy (HRTEM) and energy-filtered transmission electron microscopy (EFTEM). To obtain elemental maps, the 3-window method [10] was applied, where the intensities from the first two windows (pre-edges 1 and 2) and third window (post-edge) are used for the background subtraction and the map, respectively. The sample was stabilized for 60 min before recording, in order to minimize the possible mechanical drift of the sample stage.

When the focused electron beam position was moved into space at a certain speed (here 1.2–3 nm/s) along the edge of holey carbon film, freestanding rod-like nanostructures

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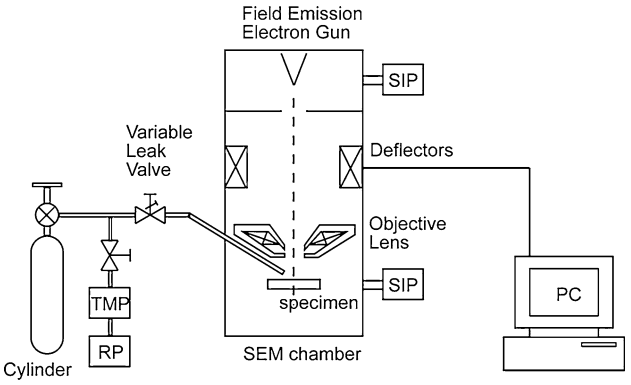

Fig. 1 The schematic of EBID experiment

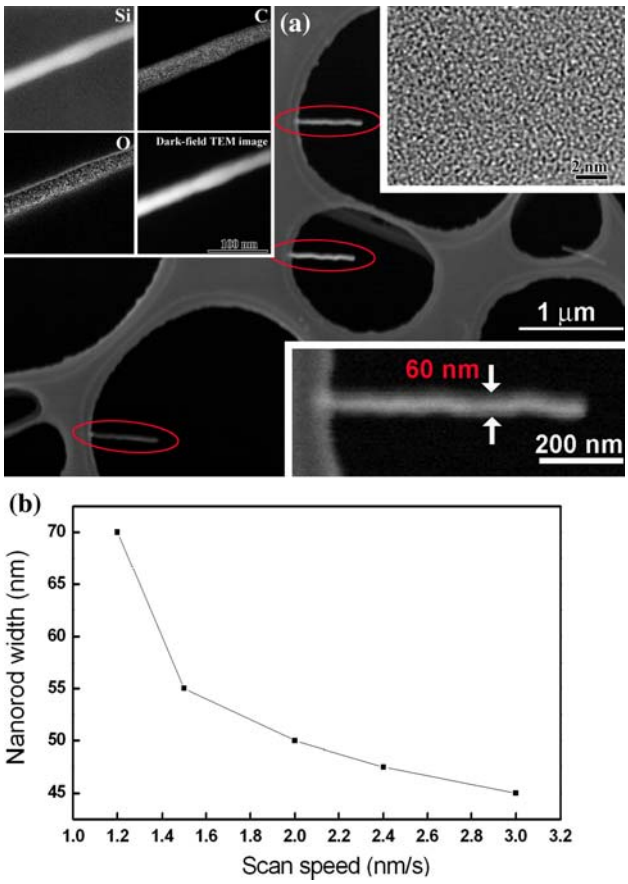

Fig. 2 (**a**) SEM image of nanorods. The bottom-right, top-right, and top-left insets are the SEM, HRTEM, and EFTEM (Si, C, and O maps as well as the corresponding dark-field TEM) images of one nanorod, respectively. (**b**) The dependence of the nanorod width on electron beam scan speed

(thereafter nanorod) were fabricated. Figure 2a is a scanning electron microscopy (SEM) image of as-deposited nanorods (see the red-circled). The nanorods are amorphous, as shown by the *top-right* inset. The *top-left* inset (elemental maps) shows that the nanorods are rich with silicon as well as some carbon and oxygen (see Table 1 for the detailed experimental conditions in EFTEM images). Such an amorphous Si–C–O structure is typical of a ceramics phase, remaining stable even after undergoing a 600 °C/1 h heating. The *bottom-right* inset reveals the width of nanorod is about 60 nm under a speed of 1.5 nm/s. The width can be flexibly controlled in a given gas pressure. Generally speaking, the larger the scan speed of electron beam is, the narrower the width of nanorod is, as shown in Fig. 2b.

In what follows, we will explore the effects of dynamic precursor gas pressure on the fabrication of nanorods in EBID. Some amount of precursor gas was introduced to the specimen chamber (say with a pressure of 1.8×10^{-4} Pa) and then the gas supply was cut off. Hence, the gas pressure was gradually reduced under the continuous consumption of gas molecules with the preceding of EBID process. Under a scan speed of electron beam 1.5 nm/s, nanorod width remains constant with an average value 59 nm, as shown in Fig. 3. The relationship between dynamic gas pressure P (10^{-6} Pa order) and the sequential numbers n of fabricated nanorods is approximately written as,

$$P = 44 + 158.2 \exp(-n/3.1). \quad (1)$$

Obviously, the gas pressure decreases quickly with the continuous production of nanorods until a saturation tendency occurred. Then the subsequent nanofabrication was terminated at $n = 20$ due to the insufficient supply of gas source.

It is known that the brightness (intensity) of the signal depends on the number of secondary electrons (SEs) reaching the detector in scanning electron microscope [11]. The relative intensity I of nanorods with similar chemical composition is just a reflection of its thickness in SEM image. In order to measure the intensities I, the intensities of dark hole where nanorods locate were initially normalized to zero. The relative intensities perpendicular to the growth direction (see the inset) were obtained for every successively formed nanorod by using their full width at

Table 1 Experimental conditions for the acquisition of elemental maps in EFTEM images

Edges	Ionization energy (eV)	Pre-edge 1 (eV)	Pre-edge 2 (eV)	Post-edge (eV)	Slit width (eV)	Acquisition time (s)
Si–$L_{2,3}$	99	88	98	115	10	15
C–K	284	236	260	284	20	15
O–K	532	480	506	532	20	15

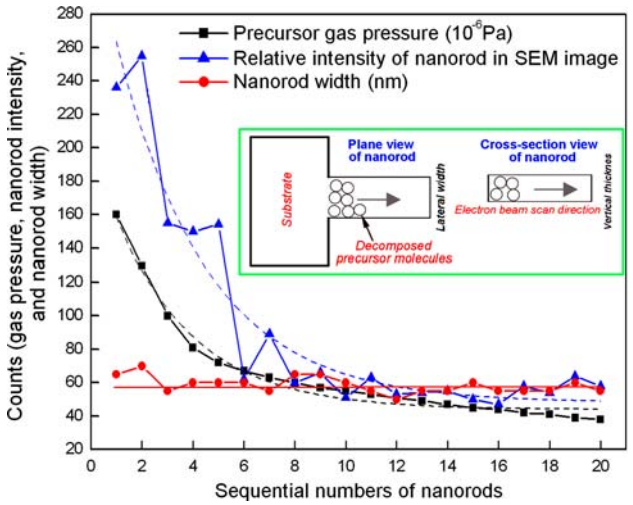

Fig. 3 The evolving of relative intensity (illustration of thickness), width of nanorod in the SEM image, and precursor gas pressure with the preceding of EBID process. Dashed curves are the corresponding simulations of these three variables. The inset is a schematic of the morphology of nanorods

half maximum. It was found that the relative intensity I of nanorods is correlated with n by an expo-decay style, similar to the play between dynamic precursor gas pressure P and n, as follows,

$$I = 48 + 285.4 \exp(-n/3.5). \quad (2)$$

Based on the aforementioned analysis, the function (2) is also an illustration of the relationship between the nanorod thickness and the sequential numbers n of fabricated nanorods. That is to say, the nanorod thickness is strongly correlated with the dynamic precursor gas pressure whereas the nanorod width is constant during the EBID process.

In EBID, primary electrons from the electron beam impact the substrate, causing the emission of SEs. It is well known that these SEs play a prominent role in dissociating adsorbed precursor molecules [4, 9], which is responsible for the formation of the ultimate nanorod. When fixing electron beam scan speed, the total amount of forward-scattering SEs from a growing nanorod should be the same at unit area. Then the width (its lateral growth, see the inset in Fig. 3) is constant in the plane view of nanorod. With more supply of gas resource for the deposition, the initial EBID process with larger gas pressure will contribute more to the thickness (its vertical growth) of nanorod than the subsequent stage with the continuous consumption of gas pressure.

In summary, we succeeded in fabricating amorphous Si–C–O nanorods by electron beam induced deposition using tetra-ethoxy-silane. With the dynamic reduction of precursor gas pressure, the nanorod thickness decreases whereas the nanorod width (controlled by electron beam scan speed) remains constant. Our work helps to design the size and control morphology of nanorods by using electron beam-induced deposition.

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