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Direct electron-beam-induced formation of nanometer-scale carbon structures in STEM.

II. The growth of rods outside the substrate

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Abstract. — Electron-beam-induced growth of self-supporting carbon-containing rods outside the substrate has been investigated. The influence of the beam current in the range of 1 to 80 pA on the shape and dimensions of the rods has been determined. Differences in rods growth at the edges of dielectric and metallic substrates have been demonstrated. Energy loss spectra have been recorded during rods formation and then analyzed. The obtained results have been ascribed to the accumulation of electrostatic charges on the formed structures.

1. Introduction

It is well known carbon-containing rods or bridges can be formed outside the substrate with focused electron beam in scanning electron microscope [1]. Hydrocarbonic layer on the substrate and oil vapour in the column of microscope are the sources of material for these rods and bridges. In the available literature possible ways for utilizing this technique in microelectronics have been suggested [2,3] and the influence of some parameters of the process on the growth of self-supporting rods has been analysed. In particular, experimental investigations have been performed, concerning the dependence of the growth of self-supporting carbon-containing rods on the electron beam displacement speed, on the temperature and material type of the substrate from which edge their growth begins [4]. It has been shown that a great number of parallel fibers placed one over another in the direction of the beam propagation may grow simultaneously [4, 5]. In accordance with the model offered in reference [6] for the explanation of this fact, the fibers originate simultaneously from certain points on the surface irradiated with the electron beam; the surface areas adjacent to them are a source of hydrocarbon molecules, which build up separate fibers.

The study of the so-called "proximity effect", associated with the change in shape and dimensions of the bridges, has considerable practical importance [2]. One of possible causes for

the observed spread may be the dissociation of hydrocarbon molecules on the surface of previously grown structures under the action of characteristic X-ray irradiation or secondary electrons (mainly Auger electrons) emitted from the end of a new bridge. The observed bending of previously formed bridges arises due to the presence of electrostatic forces [2]. Electrostatic charging also affects the processes of electron migration over the specimen surface, which control the rate of growth of carbon-containing contamination layers [7].

We have previously reported that carbon-containing ledges are formed at the rim of film substrates when the electron beam passes outside at a distance of up to 30 nm from its edge [8, 9]. The effect has been accounted for by surface plasmon excitation or direct excitation followed by the dissociation of hydrocarbon molecules on the surface.

Using the above ideas as the basis for the present paper, the electron-induced growth of self-supporting carbon-containing rods outside the substrate has been investigated, including the influence of the substrate type and of the beam current within the range of 1 to 80 pA, on the shape and dimensions of the rods formed. Energy loss spectra of primary beam electrons (EELS spectra) obtained during rods formation have been analyzed.

2. Experimental.

The experiments have been carried out in a scanning transmission electron microscope of the VG HB501 type under an accelerating voltage of 100 kV. The field emission gun can deliver an electron beam current up to 80 pA within a beam diameter of 1 nm. Oil vapor in the microscope column pumped down by oil-vapor diffusion pump and starting contamination of substrate constitute the source of hydrocarbon molecules for the formation of carbon-containing rods.

To find out the influence of the substrate electrical conductivity on electron-induced formation of carbon-containing rods dielectric and conductive substrates have been used. SiO_2 membranes 80 nm thick and Si_3N_4 layers 40 nm thick obtained on silicon were used as dielectric substrates [10]. To get conductive substrates, thin metallic layers (niobium or iron) were deposited on these membranes with cracks were selected for the experiments.

The thickness of the rods was determined from electron energy loss spectra in accordance with a well-known procedure [11].

3. Experimental results and discussion.

Figure 1 presents a typical EELS spectrum recorded during rods formation. This spectrum is similar to those acquired when the electron beam travels at a certain distance outside the carbon-containing ledge [8,9]. The energy loss peak at 20 eV substantially differs from the value of the plasmon loss when the beam passes through a carbon-containing material (25 eV) [11].

This result suggests that the beam electrons practically travel outside the rod body and the excitation of surface plasmons, not of the volume ones, prevails (17.7 eV for carbon [11]). The possibility of direct excitation of multiatomic hydrocarbon molecules present on the surface, is not ruled out [8,9]. When the rate of electron beam displacement is significantly decreased (<1 nm/s) or when the substrate has been additionally contaminated with hydrocarbon, the energy loss maximum of transmitted electrons is shifted to higher energies (22-23 eV). In this case it is evident that the main portion of electron beam is transmitted through the material of the rod formed, giving rise to the excitation of volume plasmons.

The shape and dimensions of the rods grown at the edge of dielectric substrates turn out to be considerably different from those grown off the metallic ones. When a metallic substrate is used,

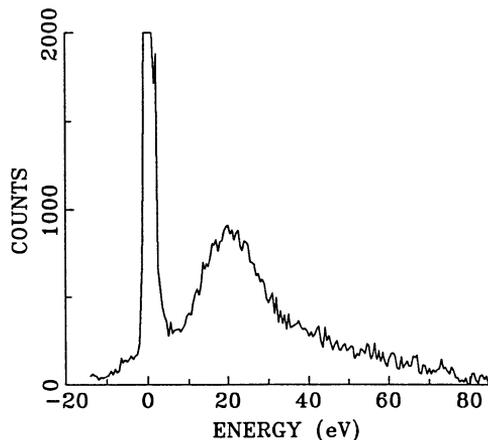


Fig. 1. — Energy loss spectrum recorded during the formation of a self-supporting carbon-containing rod. The rate of electron beam displacement is 6 nm/s, the beam current is 30 pA.

the rods grow homogeneously in width and thickness (Fig. 2a). If the rods growth takes place at the edge of a dielectric substrate, the rods are generally shorter and the splitting of the rod end into a characteristic "brush" is followed by stoppage of the growth (Fig. 2b). In other cases when the rate of electron beam displacement is below 2.4 nm/s, the rod is gradually contracted (Fig. 3). It has also been found for dielectric substrates and weak beam currents (≤ 5 pA), that such divergence is not observed or is less pronounced within the range of rate of electron beam displacement below 12 nm/s. These results can be qualitatively attributed to the accumulation of electrostatic charge at the end of the rod formed. Here the charge at the end of the rod must be positive since the action of primary beam must cause the emission of secondary electrons resulting in deficiency of negative charge [12]. When the rod formation process takes place on a dielectric substrate, the positive potential is evidently higher at the end of the fibers forming the rod. It is expected that mutual repulsion between one-sign charged fibers at a certain potential at the rod end is responsible for the splitting.

To investigate the growth kinetics of hydrocarbon rods, the transmitted current of electrons having not undergone large-angle scattering, was registered during the time of growth. Usually smooth plots of the current *versus* the growth time were observed. Sometimes characteristic aperiodic oscillations are displayed which, as a rule, precede the end of the rod growth (Fig. 4). These oscillations may result from mutual repulsion of one-sign charged fibers. The higher the potential at the end of the rod, the more intense the splitting of the fibers and the smaller the thickness of the material through which the electron beam is transmitted. This leads to a decrease in electron scattering events and hence to a decrease in secondary emission which in turn decreases the potential at the end of the rod and also the fibers splitting. A certain cyclicity of the process follows from its nature. In some cases the oscillation of the current of transmitted electrons arises due to irregular and heterogeneous growth of carbon-containing rods. But here the current oscillations do not precede the growth stoppage and are observed over the whole length or growing rod. In this case the photographs show irregularities of the rods both in thickness and in width.

For self-supporting rods on dielectric and metallic substrate, differences have also been found concerning the "proximity effect". When metallic substrates are used, the deformation (bending) of the already formed rods occurs during the growth of a new rod at a distance of some hundred nanometer from them only (Fig. 5), the bending being always directed towards the second growing

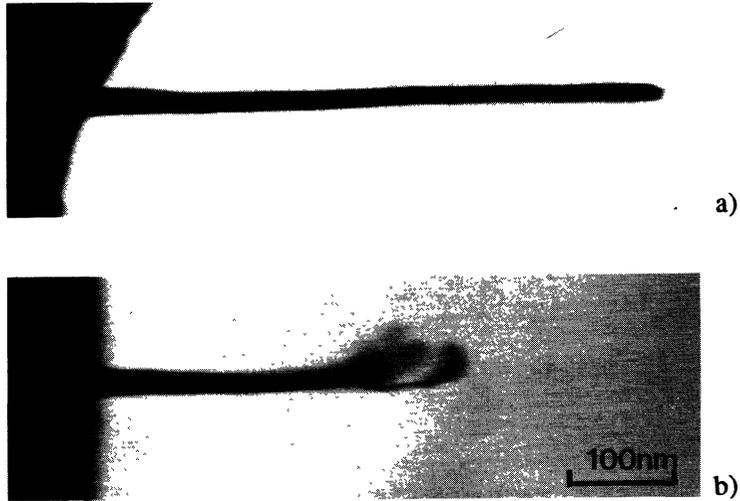


Fig. 2. — Images of self-supporting carbon-containing rods grown from the edge of a metallic substrate (a) and from the edge of a dielectric substrate (b). The rate of electron beam displacement is 3 nm/s, the beam current is 30 pA.



Fig. 3. — Image of self-supporting carbon-containing rods grown from the edge a dielectric substrate. The rate of electron beam displacement is 2.4 nm/s, the beam current is 50 pA.

rod. The greater the distance between the rods, the lower the value of the broadening and bending of the first of two rods. But if the rod grows from the edge of a dielectric substrate, its broadening (however smaller than in the case of a metallic substrate) is not accompanied by the bending effect (Fig. 3).

Figure 6 shows a microdensitometer trace across rods 50 nm apart. It is obvious that the left profile corresponding to the first rod is asymmetrical: the broadening always occurs on the side facing the second rod. As it has been mentioned above it was supposed [2] that contamination broadening is mainly due to Auger electrons. At the same time theoretical estimations [13] and experimental data [14] show that slow secondary electrons may play a leading role for a certain type of chemical bonds. In this case it should be remembered that the flow of emitted true secondary electrons exceeds by some orders of magnitude the flow of emitted Auger electrons. Therefore it

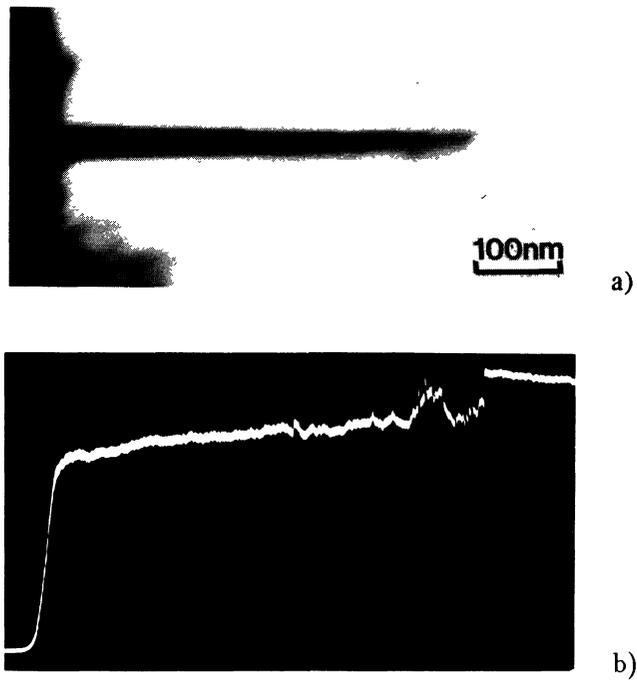


Fig. 4. — Images of a carbon-containing rod grown from the edge of a dielectric substrate (a) and the associated dependence for the current of electrons having not undergone elastic large scattering on the rod growth time (b). The rate of electron beam displacement is 12 nm/s, the beam current is 30 pA.

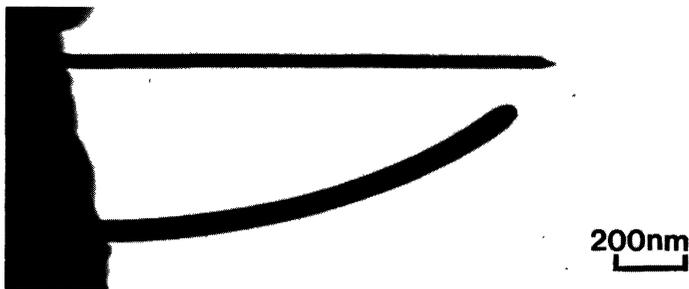


Fig. 5. — "Proximity effect" for self-supporting carbon-containing rods grown from the edge of a metallic substrate. The rate of electron beam displacement is 4.8 nm/s, the beam current is 50 pA.

is believed that the profile asymmetry may be caused by the dissociation of hydrocarbon molecules on the first rod surface under the action of true secondary electrons emitted from the end of the second rod during its growth. It is quite possible that a contribution to the asymmetry is made by electron-stimulating desorption of positively charged hydrocarbon radicals from the end of the rod formed which then deposit on the elements already formed nearby.

The presence or the absence of the bending of previously formed rods or bridges (see Fig. 2

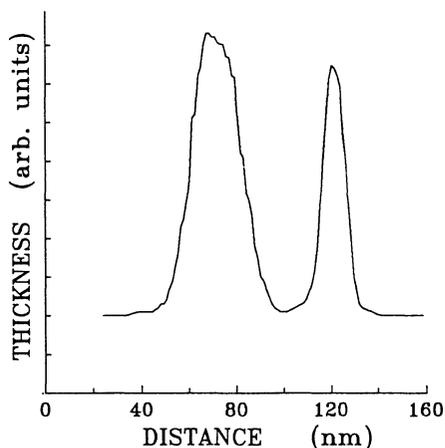


Fig. 6. — Microdensitometer trace across rods 50 nm apart. The rate of electron beam displacement is 6 nm/s, the beam current is 50 pA.

in [9]) can be explained by two causes. One of them is the following. A fraction of secondary electrons emitted during the formation of the second rod reaches the first one charging it negatively (Fig. 7). When conductive substrates are used, the current flows along the rod and compensates for the rod charges resulting from the secondary electron emission from the end of the second rod. The emitted secondary electrons are accumulated on the first rod. Electrostatic attraction between the positively charged second rod and the negatively charged one obviously leads to bending of the first rod to the growing one. If a dielectric substrate is used, the emission of the secondary electrons from the end of the second rod decreases due to the increase of its positive potential. As a result the decreasing current of the secondary electrons emitted from the end of the growing rod seems to be compensated by the current of positive ions which are desorbed from it and reach the first one. As a consequence the absence or small value of the charge on the first rod and hence the absence of its bending can be expected.

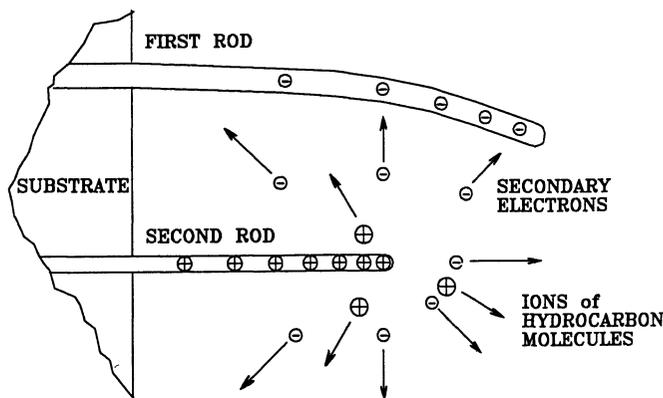


Fig. 7. — Schematic diagram to explain the bend of the first rod.

Another possible cause is the formation of cross-links in the polymer by bombardement of the surface of the first rod by secondary electrons emitted from the end of the growing rod [15]. This effect may induce the deformation contraction (compression) of the rod material surface layers facing the growing rod, leading to the bend of the first rod. Irreversibility of the bend (the rods do not unbend when they become electroneutral) may be the confirmation of such a mechanism. Note that the bends of the rods (e. g. caused by electrostatic force) may also be fixed by the polymer film formed on the curved surface due to the dissociation of carbon molecules migrating over the surface.

The foregoing shows that electrostatic effects are essential and must be taken into account when analysing the electron-induced growth of self-supporting carbon-containing structures (rods, bridges, etc). This consideration is useful to explain the apparently contradictory experimental dependences of the thickness and width of the rods on the electron beam current. Originally it has been determined that the thickness and width of growing rods decreases with increasing beam current [16]. This process cannot be attributed to thermal-stimulated desorption of hydrocarbon molecules because simple estimations show that the heating of the rod end by the electron beam energy is practically absent within the used beam current range.

Actually within a rather wide range of beam currents the dependence of the thickness h of the rods on the beam current I turned out to be more complex. Figure 8 shows the results for beam currents ranging from 1 to 80 pA. The plot can be divided into three regions. From zero to 5 pA the thickness increases with the current. The process is obviously determined by the number of dissociation events of hydrocarbon molecules excited by the beam electrons on the surface. For currents above 30 pA, the fixed thickness can be explained by the fact that surface diffusion limits the delivery of hydrocarbon molecules into the reaction zone [17].

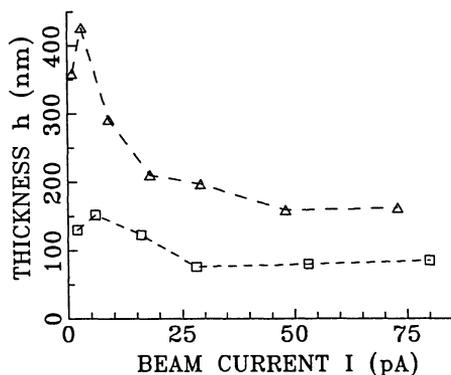


Fig. 8. — Thickness h of carbon-containing rods formed behind the edges of metallic (Δ) and dielectric (\square) substrates versus the electron beam current I . The rate of electron beam displacement is 3 nm s^{-1} .

For intermediate currents (from 5 to 25 pA) the thickness of growing rods decreases with increasing current. This may be caused by the following. Electron-induced excitation of hydrocarbon molecules results either in dissociation or in ionization. In the latter case the probability of ion desorption obviously increases as compared to neutral molecules because of the electrostatic repulsion of positive ions from positively charged rods. At high field intensity the effects connected with field desorption of hydrocarbon molecules from the surface of growing rod may play a significant part [18]. In the point charge approximation when the potential at the rod end is

10 V and the fiber radius is 10 nm, the electric field intensity is estimated $\approx 10^9$ V/m. Over the current range under consideration desorption rate of positive ions increases with increasing rod charge. It is evident that ion desorption will finally lead to the decrease in surface concentration of hydrocarbon molecules and their total dissociation rate and hence to the decrease in the rod thickness. The estimations show that the fraction of secondary electrons emitted from the surface decreases as positive potential at the end of the rod increases. Consequently the potential at the end of the rod does not increase in proportion to the beam current but approaches asymptotically a constant value which seemingly does not exceed a few tens of volts.

It should be noted that there is qualitative similarity between the dependences of the thickness on current when metallic and dielectric substrates are used (Fig. 8).

4. Conclusions.

The following results and conclusions have been obtained:

1) EELS spectra exhibit a dominant peak at 20 eV during the formation of self-supporting carbon-containing rod. Such a value suggests that the electron beam passes practically outside the rod body formed beyond the substrate and in this case directly excites surface plasmons or hydrocarbon polyatomic molecules.

2) It has been found that the shape and dimensions of the rods from the edge of dielectric and metallic substrates are different. When the rods grown from the edge of a dielectric substrate reach a particular length, their extremity is splitted into separate fibers and the growth stops.

3) For both types of substrates, the broadening of previously formed bridges or rods is observed when a new element grows in close proximity to them; in the case of metallic substrates, the formerly grown rods bend. The secondary emitted electrons during the growth of the second rod may be responsible for these "proximity effects".

4) The dependence of the thickness of the rods has been measured for beam currents between 1 to 80 pA. Two regimes have been observed: thickness increases with current from 0 to 5 pA and then decreases with a further increase of current from 5 to 25 pA. These behaviours can be explained by the desorption of hydrocarbon molecules from the end of positively charged rods. These investigations demonstrate that STEM-techniques are a powerful tool for the fabrication of self-supporting nanometer-size structures which could be used in nanoelectronics as the substrate structures. Further studies will be necessary in order to develop this method for some particular application.

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