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Electron-Beam-Induced Fabrication of Metal-Containing Nanostructures

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Summary: An experimental system based on a transmission electron microscope JEM-100CX has been developed for electron beam-induced chemical vapor deposition. Direct electron beam-induced growth of nanometer-wide self-supporting rods has been performed inside the microscope operating in scanning mode by decomposition of carbonyls of chromium $Cr(CO)_6$, tungsten $W(CO)_6$, and rhenium $Re_2(CO)_{10}$. In situ phase and structure transformations under annealing inside the microscope column were studied. Nanoscale rods and strips grown from rhenium carbonyl are of special interest because, after annealing, they consist of a single pure rhenium phase. The described method of metallic nanoelements fabrication enables us to produce highly conductive nanowires and tips for application in nanoelectronics, emission electronics, and scanning tunneling microscopy.

Key words: electron beam-induced CVD, metal-containing nanostructures, nanoelectronics

Introduction

Submicron-sized elements are of great interest in physics and technology. A variety of methods exists to produce them by both conventional microelectronics technology and new methods for the deposition of such elements, consisting of a desired material, onto a substrate. The current one-stage maskless techniques of laser-induced chemical vapor deposition (CVD) and laser-induced etching (Rotshild and Ehrlich 1988) do not ensure resolution below 250 nm because of their physical limitations imposed by the laser wavelength. Focused ion beams, which generally allow the formation of submicron-sized elements, are often unacceptable because they can cause radiation damage in the material. On the other hand, electrons with an energy up to 100 kV do not cause radiation damage in most materials (Hobbs 1979). Moreover, scanning transmission electron microscopes (STEM) are very well suited because of their fine electron beam (in conventional STEM the beam diameter is 2–3 nm) and feasibility of exact beam position control. The use of scanning electron microscopes for fabrication of structures with required configurations by an electron-beam-induced dissociation of oil molecules on a substrate has been reported by several authors (Aristov *et al.* 1992, Kislov 1993, Mueller 1971). This particular technique allows the direct formation of only carbon-containing structures. Further development of electron-beam-induced CVD-based techniques comprises the formation of submicron-sized patterns from various materials directly on the substrate (Koops *et al.* 1988, Matsui and Mori 1985).

The process is as follows: A vacuum chamber is filled with metal carbonyl or metal organic compounds vapor at an appropriate pressure, while an electron beam is moving across the surface of the substrate onto which the desired nanostructure has to be grown. Adsorbed molecules, diffusing along the surface with a strong gradient towards the incident beam, are dissociated by the incoming electrons. Parts of their breakdown products form an immobile deposit at the momentary beam site. A strip continues to grow even after the beam moves away from the substrate into vacuum, thus forming a self-supporting nanostructure.

A wide range of applications of this kind of technique is expected in nanotechnology. A corresponding, similar attempt to use an electron beam-induced CVD technique to produce tips for scanning tunneling microscopy (STM) was reported by Huebner *et al.* (1992). However, it has not been conclusively proven that those fabricated tips provided the necessary electrical conductivity for routine STM applications. The electric resistivity of the fabricated material was by far too large to regard it as a conductor (approximately 400 Ω cm), thus stimulating a search for new kinds of materials and technological treatments to produce sufficiently conducting nanometer-scale wires. There have been no prior reports about additional treatments, vacuum annealing in particular, carried out to

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change the structure of a material deposited by the electron beam-induced nanodeposition method.

This paper deals with a novel technique of electron beam-induced CVD from metal carbonyl $Cr(CO)_6$, $W(CO)_6$, and $Re_2(CO)_{10}$ vapors, including for the first time further structural transformation of nanometer-scale self-supporting rods by their annealing subsequent to deposition.

Experimental Procedure

The CVD experiments were performed in a TEMSCAN JEM-100CX electron microscope at an accelerating voltage of 100 kV. The electron microscope was equipped with a specially designed holder connected with the oil-free system for pumping and the reagent vapor inlet (Fig. 1). This allowed the maintenance of a well-defined atmosphere of chemical compounds (metal carbonyls, halides, freons) around the specimen. Two electronically controlled needle valves were capable of supplying two different reagents simultaneously into the specimen holder. The sample was placed inside the holder heater that provides temperatures up to 250°C required for the local electron beam-induced etching. The holder was supplied with an electrical lead-in that allowed in situ measurements of electrical characteristics of a sample. The holder had two differential apertures (through which the electron beam passes) placed above and beneath the sample. These apertures kept the gas pressure around the sample in a range up to 1 Pa without breaking the vacuum in the microscope column. A direct measurement of the gas pressure right around the sample is technically complicated; however, its value could be estimated from the readings of the manometer placed at the outlet of the gas supply system and a calculated pipe resistance of the vacuum system (Dushman 1962). A computer was used to control the beam position in the microscope via 16-bit digital-analog x-y boards.

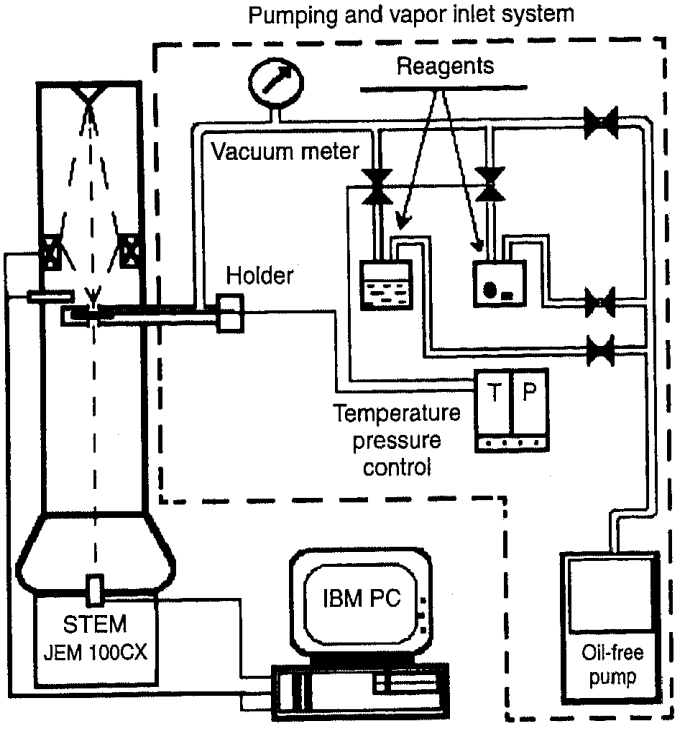

FIG. 1 Schematic diagram of the high-resolution electron-beam-induced CVD system.

Self-supporting rod growth from all of the metal carbonyls was started from the silicon edge formed by {III} planes with an interfacial angle about 71° as a consequence of selective etching of square window in silicon wafer (Enquist and Spetz 1986) followed by chemical removing of the Si_3N_4/SiO_2 film.

Structure and composition analyses were both performed in a JEM-2000FX electron microscope equipped with a Link AN-10000 system for energy-dispersive x-ray (EDX) analysis.

A preliminary treatment of the substrate holder cage as well as of the silicon substrates themselves was performed comprising two steps: cleaning in organic solvents (acetone, CCl_4) and baking at 200°C for 1 h in ambient atmosphere to decrease carbon contamination during nanostructure deposition. In our experimental conditions, the growth of self-supporting carbon rods at room temperature was interrupted at a typical beam displacement velocity of about 1 nm/s. Thus, beam displacement velocities higher than 4 nm/s were chosen in all further experiments to decrease carbon contamination.

Results and Discussion

Self-supporting rods 20–100 nm wide, consisting of rhenium, chromium, and tungsten, were grown up to 8000 nm long at velocities of the electron-beam movement between 5 and 10 nm/s and at a vapor pressure of 0.01 Pa near the sample. Figure 2a displays a common view of typical self-supporting rod grown from the atmosphere of carbonyl tungsten. The EDX spectrum peaks of the rod in Figure 2b indicate, in particular, the presence of tungsten as a product of electron beam-induced transformation of the $W(CO)_6$ molecules.

From the tilting experiments in the transmission electron microscopy (TEM) mode (Fig. 3b), our self-supporting rhenium-containing rods appear being made up from several individual fibers mutually aligned in parallel. The morphology of the Re-nanorods, thus, is similar to that of the well-known carbon rods and may be explained based on the Moellenstedt idea about the existence of a circular area depleted from diffusing surface molecules around the special spots of the filaments nucleation, and the distance between growing in sequence filaments is determined by the radius of the depleted region (Kreuzer 1988, Moellenstedt 1988).

However, we did not observe multiple fiber growth either at tungsten-containing or at chromium-containing rods in numerous experiments with $W(CO)_6$ and $Cr(CO)_6$ vapor sources. The reason of this may be in a high chemical barrier for nucleation under autocatalytic thermal decomposition of the VIB group metal carbonyl molecules (Kunz and Mayer 1988).

The selected area diffraction (SAD) patterns in Figures 4a (Cr-rod) and 5b (W-rod) exhibit more sharp rings than typical diffraction patterns from the corresponding amorphous mate-

rials. These SAD patterns suggest a medium-range ordering which points to cluster formation during the electron beam-induced CVD process. The photographs of the rod microstructures in Figures 3a and 5a also show a nonuniform contrast that could be explained by the cluster structure of the materials formed. These results are in good agreement with in situ TEM observations of the tungsten cluster growth on a Si surface using a WF_6 source (Matsui and Ichihashi 1988).

In situ annealing of the metal-containing rods in the heating holder inside the microscope column transforms the medium-range ordered structure into a nanocrystalline structure. The onset of the diffraction ring sharpening was observed at 400°C for Cr, and at 600° for W and Re after 15 min of annealing at these temperatures.

After annealing at 800°C for 1 h, the different materials investigated revealed individual peculiarities: rhenium- and tungsten-containing rods transformed into nanocrystals up to 20 nm in size (Fig. 3b and 5d), whereas chromium-containing rods converted into nanocrystalline regions of much finer size (Fig. 4c). The processed corresponding SAD patterns show the dissociation of $Re_2(CO)_{10}$ leading to the formation of a single-phase deposit containing only pure rhenium (Fig. 3c). A more complicated SAD pattern for rods grown from $W(CO)_6$ vapor can be identified as containing tungsten carbide W_2C and tungsten oxide W_3O in addition to pure crystalline tungsten (Fig. 5c).

The SAD patterns of the W-containing nanorods in the present work differ considerably from our previous results which prevented us from identifying them as well- known tungsten-

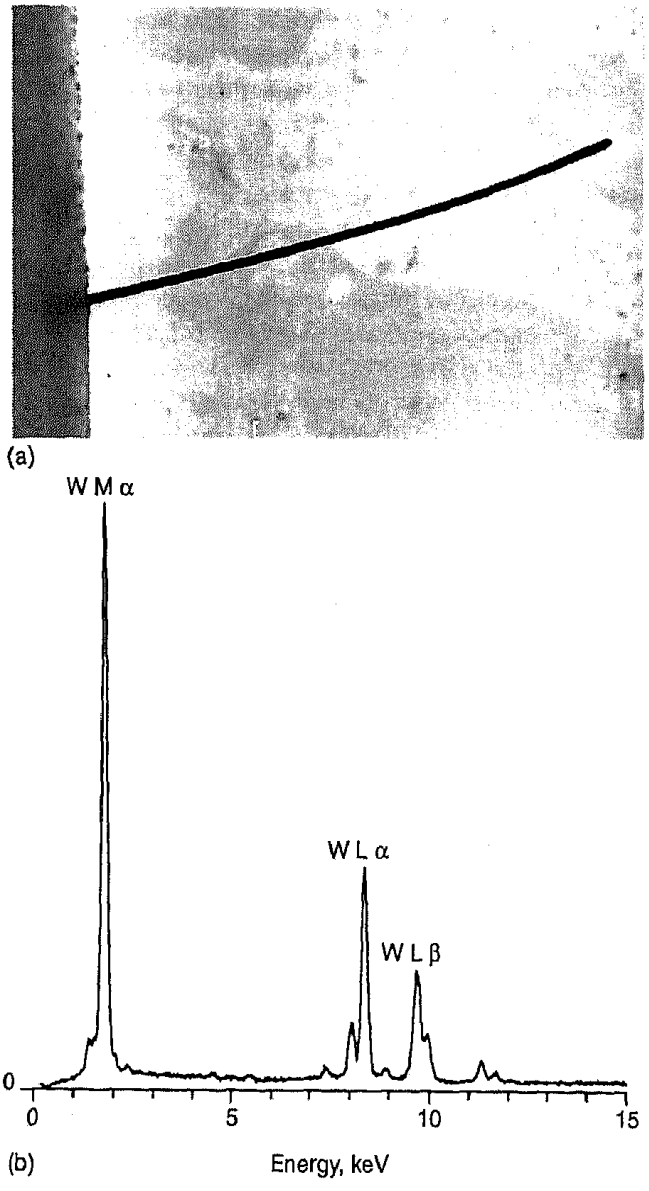

FIG. 2 Electron micrograph of a typical self-supporting rod grown from the vapor of $W(CO)_6$ (a) and energy dispersive x-ray spectrum of the rod (b). Horizontal field width for (a) = 8 μm.

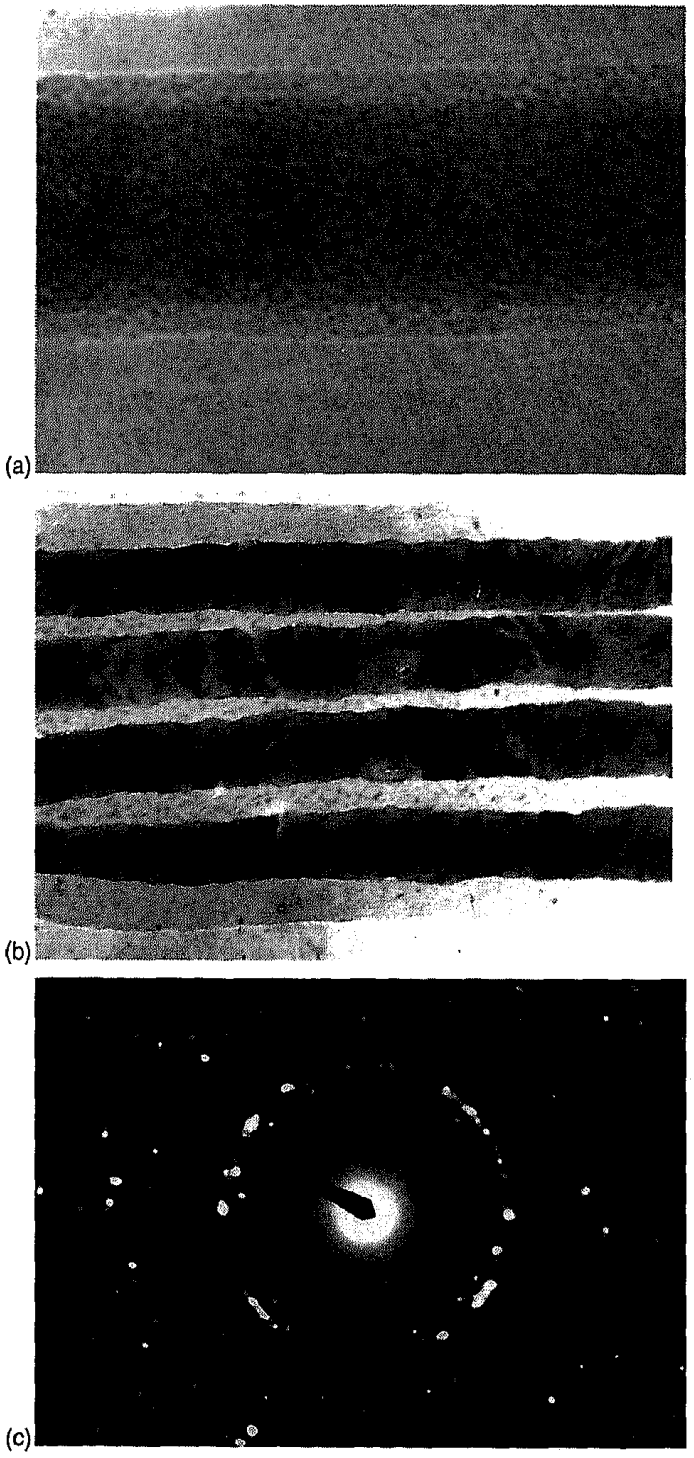

FIG. 3 Electron micrographs of rhenium-containing rods before annealing (a) and after vacuum annealing at 800°C, 1 h (b); electron diffraction pattern from the annealed rod (c). Horizontal field width for (a) = 120 nm and for (b) = 160 nm.

containing phases (Kislov *et al.* 1994). The differences may be caused by the carbon contamination and residual oxygen in the gas inlet system that were not checked in our preceding experiments.

The SAD pattern of the nanorod grown from $Cr(CO)_6$ vapor appeared very difficult to interpret (Fig. 4b). Using x-ray powder data file (Smith 1960), we could not identify any of the well-known chromium-containing phases, except a pure crystalline chromium phase. Among other lines, a cubic phase with the lattice constant 0.35 ± 0.10 nm can be identified. This result may be explained by the strong chemical reactivity of chromium, as well as by the instability of highly excited and ionized products created during electron beam-induced decomposition of $Cr(CO)_6$ (Bidnosti and McIntyre 1967).

It was observed after annealing that the rods were covered by a layer of lighter material 15–20 nm thick (Fig. 3b). The formation of the layer may be explained by the oxidation of the metal-containing rods with the residual oxygen in the column of the electron microscope. A first application test of rhenium-containing nanorods of the described kind has been performed successfully. The microtip-shaped end of the rod served as an emitter in an experimental field emission electron source (Fig. 6). The emitter was found capable of providing total emission currents up to 100 nA at an extraction voltage as low as 150 V when positioned in front of a plane anode

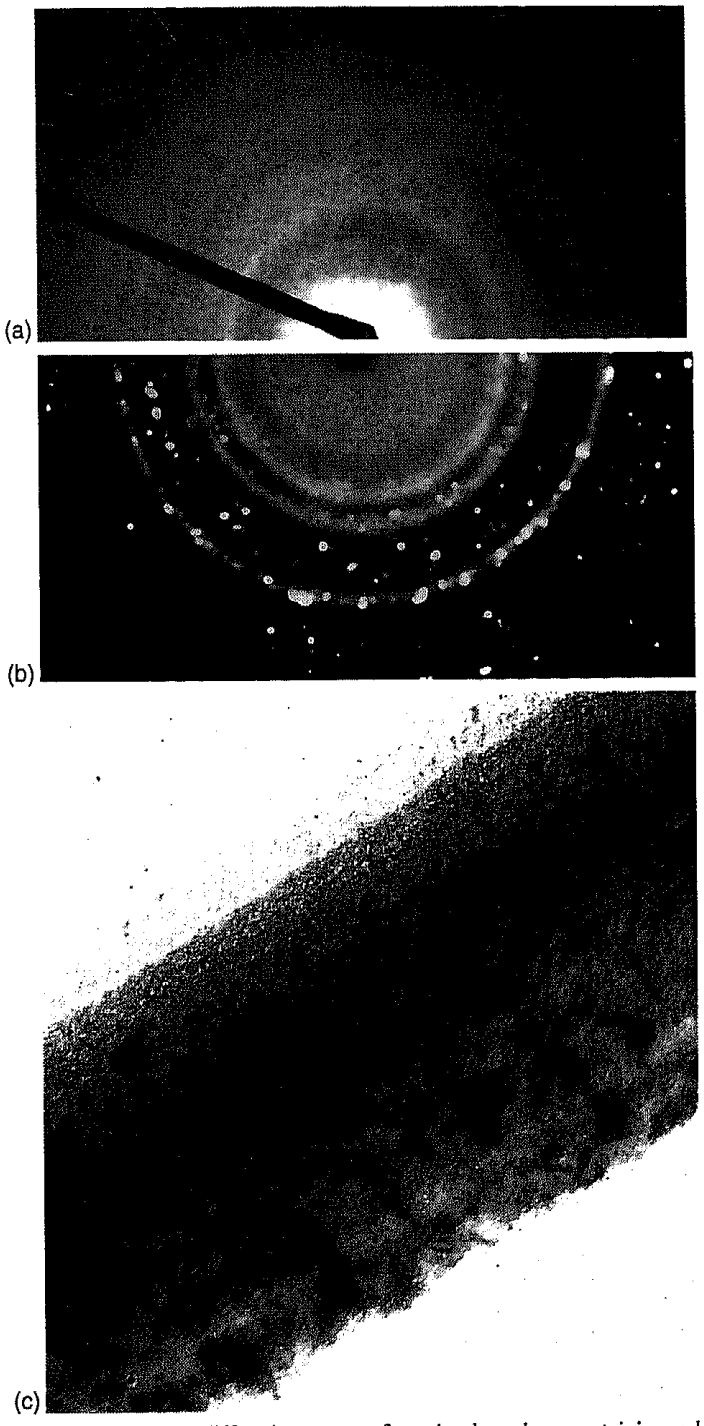

FIG. 4 Electron diffraction patterns from the chromium-containing rod before annealing (a) and after annealing at 800°C, 1 h (b); electron micrograph of the annealed rod (c). Horizontal field width for (c) = 160 nm.

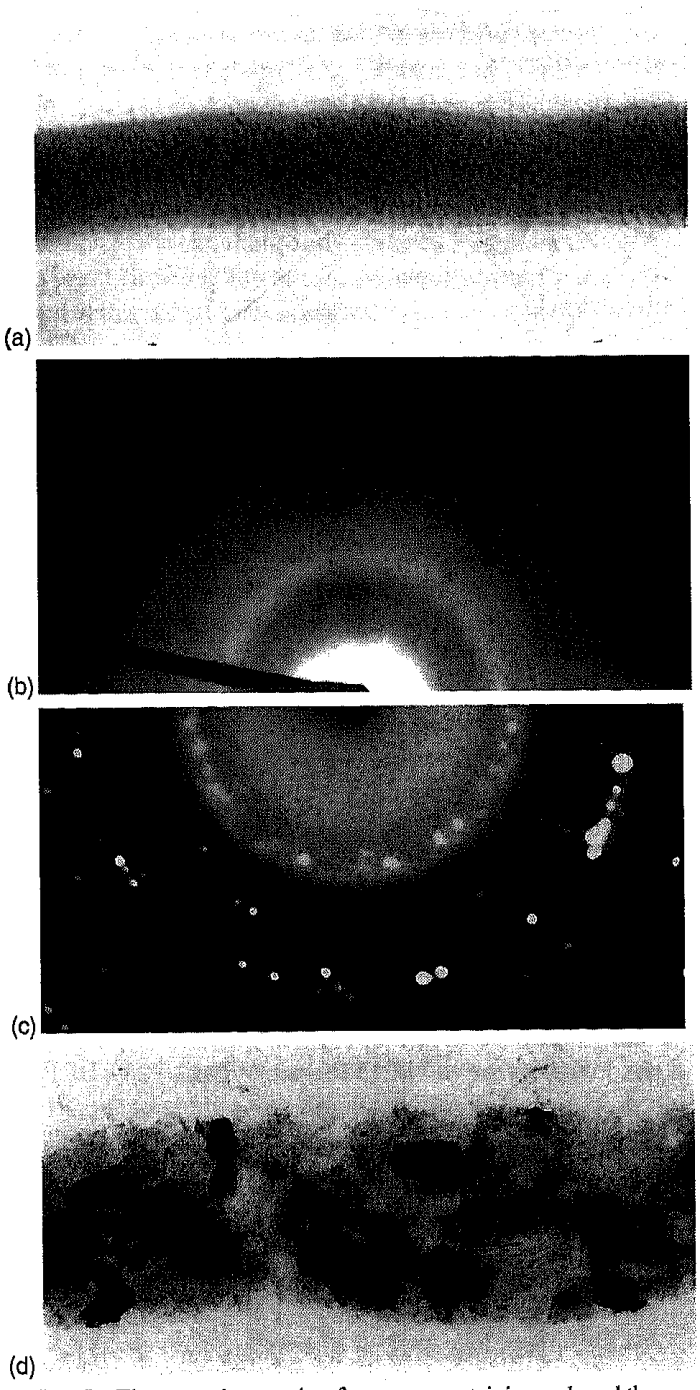

FIG. 5 Electron micrographs of tungsten-containing rods and the corresponding electron diffraction patterns before annealing (a, b) and after vacuum annealing at 800°C, 1 h (c, d). Horizontal field width for (a) and (d) = 160 nm.

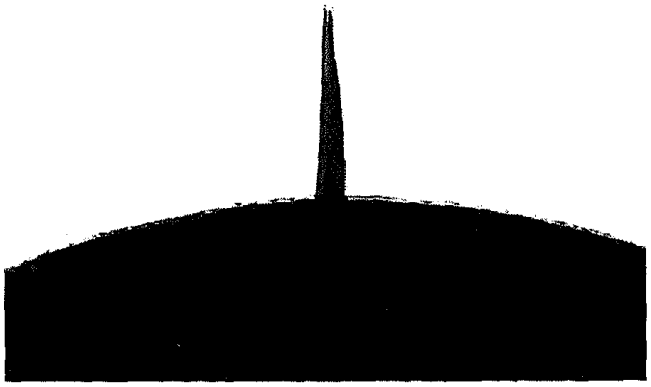

FIG. 6 Rhenium tip for testing as field electron emitter deposited on the sharpened and bent end of a tungsten wire. Horizontal field width = 4 μm.

under ultrahigh vacuum (1×10^{-8} Pa) conditions (Kirschner and Schmidthals 1994).

Conclusions

A direct electron beam-induced growth of self-supporting rods of nanometer width has been performed by decomposition of carbonyls of Cr, W, and Re.

A multiple filament structure of Re-rods was observed in contrast to the single fiber structure for W- and Cr-rods. The SAD pattern of the rods as well as their corresponding TEM images suggest a medium-range ordering in their structure that may be explained by the cluster structure of the materials formed.

In situ annealing of the rods at 800°C for 1 h inside the microscope column shows that (a) the medium-range ordered structure transforms into the nanocrystalline one; (b) the Re rods consist of only one pure crystalline rhenium phase; (c) the W rods contain tungsten carbide W_2C and tungsten oxide W_3O phases, in addition to pure crystalline tungsten; and (d) the Cr rods contain some cubic phases with the lattice constant 0.35 ± 0.10 nm and some unidentified phases, in addition to the pure crystalline chromium phase.

Nanostructures fabricated by electron beam-induced CVD, especially those from rhenium, appear to be well suited for application in nanoelectronics, low-voltage field emission electron optics, and scanning tunneling microscopy.

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