EFFECT OF ULTRAVIOLET RADIATION ON STRUCTURAL PROPERTIES OF NANOWIRES

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ABSTRACT

Copper nanowires were prepared through electrochemical template synthesis using Nucleopore polycarbonate membranes having nominal pore sizes of 800nm and 15nm diameter. The 800nm and 15nm nanowires thus grown were viewed under SEM and TEM respectively, while their FCC crystallographic structure was confirmed through X-ray and electron diffraction patterns. The X-ray diffraction peaks indicated strong texturing for (200). The texturing was found to reduce significantly upon exposure to ultraviolet radiation.

KEYWORDS

Nanowires, Template Synthesis, Texturing, Ultraviolet.

1. INTRODUCTION

Nanofabrication techniques offer remarkable miniaturization potential, which is essential for further growth of the electronics industry. While refinements in various photolithography and vapour deposition techniques have been responsible for the tremendous progress made by this industry over the past half century, further development in this field calls for various technological breakthroughs, including further miniaturization of the metal interconnects. Owing to its favourable mechanical, thermal and electrical properties, along with low electromigration problems, copper has been gaining popularity over aluminium as an electric interconnect material in the semiconductor industry [1]. Copper nanowires hold the potential to serve as interconnects in futuristic nanoelectronic devices [2].

Polycrystalline materials, such as copper consist of many small crystallites or grains, compactly assembled to form the bulk material. The intrinsic properties, viz. piezoelectric constant, elastic coefficients, thermal coefficients etc. are usually anisotropic within a crystallite, i.e., the values of these properties are different along different crystallographic directions. At macro scale, these properties will follow isotropic distribution if the bulk material contains a very large number ($\sim 10^{10}$) of grains with equal probability of orientation in any direction, but will turn out to be anisotropic in case of strongly textured materials [3,4]. Preferred crystallographic orientation, or texture, usually results from the history of material processing. As a consequence thereof, the properties important from engineering perspective, as well as their degree of isotropy are governed to a great extent by the underlying crystallographic structure [5]. The effect of any bias in crystal orientation on material properties would be much more prominent in case of nano-scale components owing to their small overall dimensions and associated much smaller number of crystallites. Accurate measurement of texture is therefore essential for ascertaining the performance of fabricated nanocomponents. Though, an accurate measurement of texture requires specialized equipment [6], but the present work involves only preliminary investigations using a conventional powder X-ray diffractometer [7].

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2. CHARACTERIZATION AND ANALYSIS

The fabrication of copper nanowires was carried out through electrochemical deposition of elemental copper into the pores of Nuclepore polycarbonate membrane, which covered the cathode during the deposition process. Two different types of membranes, having pore diameters of 800nm and 15nm, pore density of $10^8/cm^2$ and 11 μm thickness each were employed as templates. The layout design of the electrochemical cell, along with other relevant details of the technique can be referred from earlier work [8].

To start the fabrication process, the cell is filled with freshly prepared and filtered electrolyte, comprising of 2.5N (200g/l) $CuSO_4.5H_2O$ dissolved in double-distilled, de-ionized water at room temperature (35˚C). Current density of 8 to 10 mA/cm^2 was kept during deposition process.
The morphological examination of the 800nm diameter wires was done under Joel, JSM 6100 scanning microscope at an accelerating voltage of 20 kV (refer Figure 1).

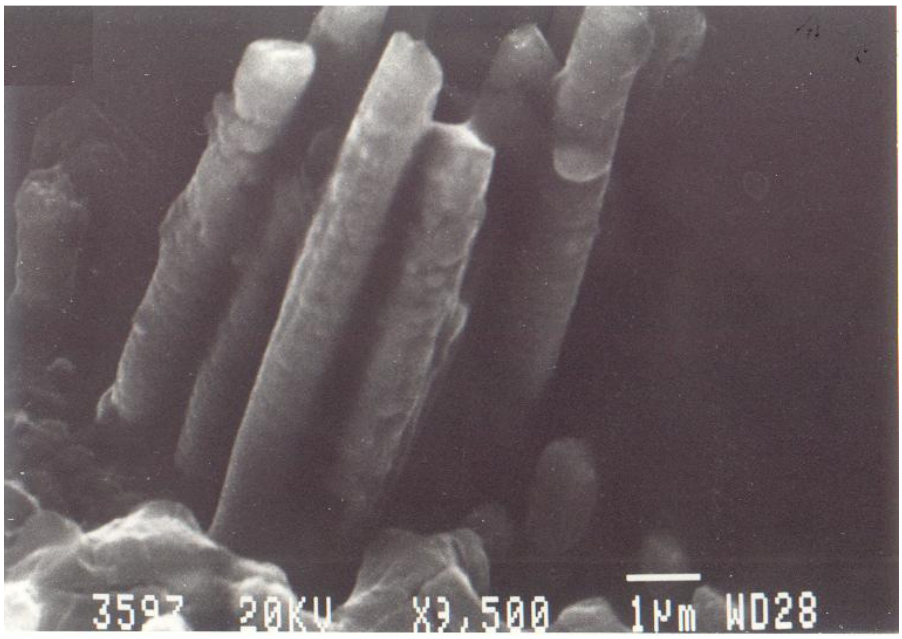

Figure 1. SEM image showing 800nm copper nanowires

Owing to their smaller size, the 15nm copper nanowires were viewed under FEI Tecnai 20 G2 S TWIN transmission electron microscope, operated at 200kV (Refer Figure 2). The transmission high energy electron diffraction (THEED), or commonly known as selected area electron diffraction (SAED) pattern was also obtained in the transmission electron microscope and is shown Figure 3.

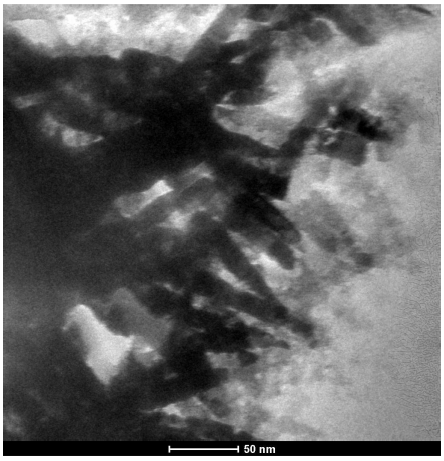

Figure 2 TEM image showing 15nm copper nanowires

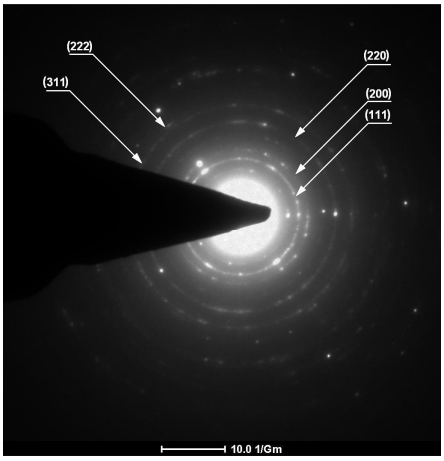

Figure 3. SAED pattern for 15nm copper nanowires

In order to carry out X-ray diffraction analysis of the deposited nanowires, the polycarbonate membranes containing nascent nanowires were peeled-off from the cathode and mounted in specimen holder of D/Max Rint 2000 Rigaku (Tokyo) X-ray diffractometer. The X-ray diffractograms obtained for 800nm and 15nm nanowires are shown in Figure 4 and Figure 5 respectively, while the application of extinction rules for identification of peaks is summarised in Table 1. As can be inferred from these diffractograms, both types of nanowires exhibited strong texturing for (200) plane.

Table 1: Identification of diffraction peaks

2θ	$\sin^2\theta$	Ratios	Normalized Ratios	Lattice Planes
43.26	0.1359	1	3	(111)
50.28	0.1805	1.33	3.98 ~ 4	(200)
73.98	0.3620	2.66	7.99 ~ 8	(220)
89.84	0.4986	3.67	11.01 ~ 11	(311)

Subsequent to recording of the X-ray diffractograms, the nanowires were irradiated with ultraviolet radiation for a period of 10 minutes using a pulsed nitrogen laser source having an output power of 10kW, emission wavelength of 337.1nm and a pulse width of less than 10ns, which corresponds to an intensity of around $2\text{x}10^9$ W/m^2 over the beam cross-section of 2x3mm, while the wavelength corresponds to a photonic energy of $hc/\lambda = 5.9\text{x}10^{-19}$J or 3.68eV. This energy can cast various pyrolytic as well as photolytic effects, viz. localized heating of surface layers, degradation of polycarbonate membrane, in particular, by breaking the C-C bonding, as the bond energy for these bonds is less than the energy of photons [9], formation of oxides or hydroxides over the regions exposed to atmosphere [10,11] and finally, in view of the high intensity of laser radiation, absorption of photons by electrons and subsequent localized rise in temperature, thereby paving the route for local recrystallization [12].

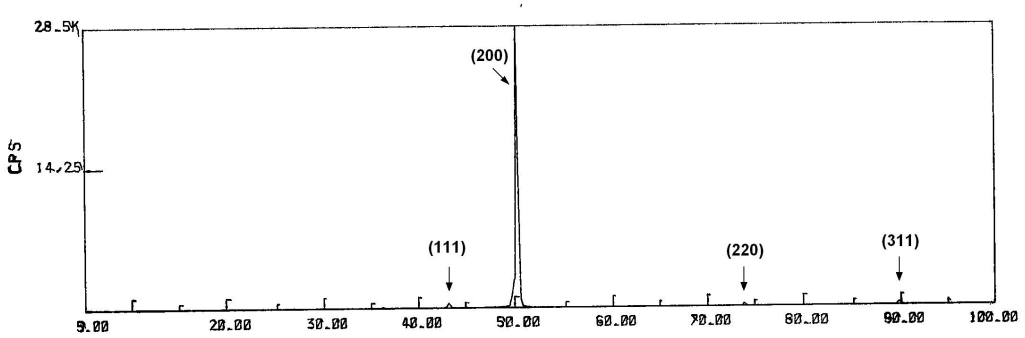

Figure 4. X-ray diffractogram of copper nanowires deposited in membrane having pore diameter of 800nm. (Before ultraviolet exposure)

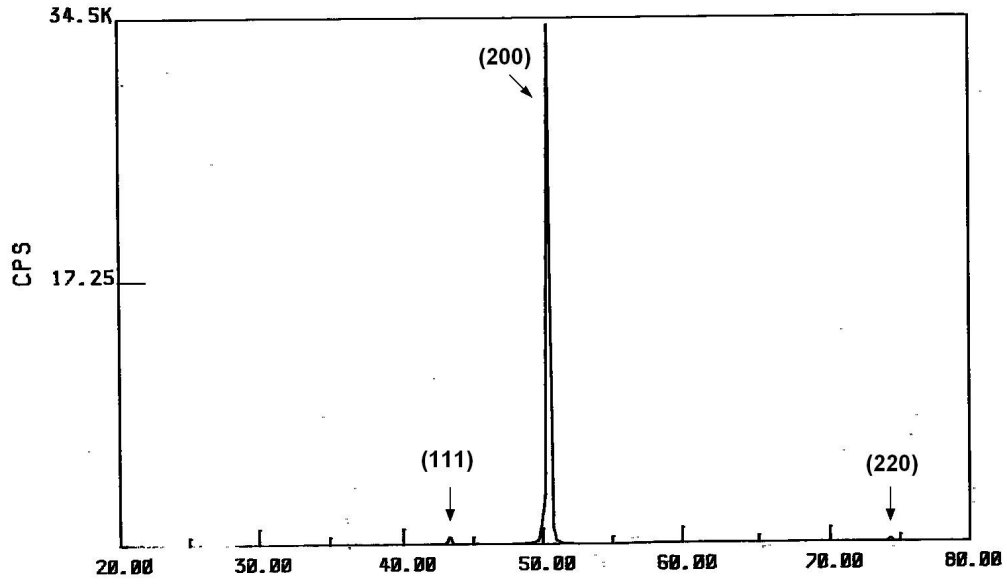

Figure 5. X-ray diffractogram of copper nanowires deposited in membrane having pore diameter of 15nm. (Before ultraviolet exposure)

In order to investigate the effect of exposure to ultraviolet radiation on the crystallographic structure of nanowires, the specimens thus irradiated were again mounted on X-ray diffractometer for diffraction analysis. The resulting diffractograms corresponding to 800nm and 15nm nanowires are shown in Figure 6 and. Figure 7 respectively.

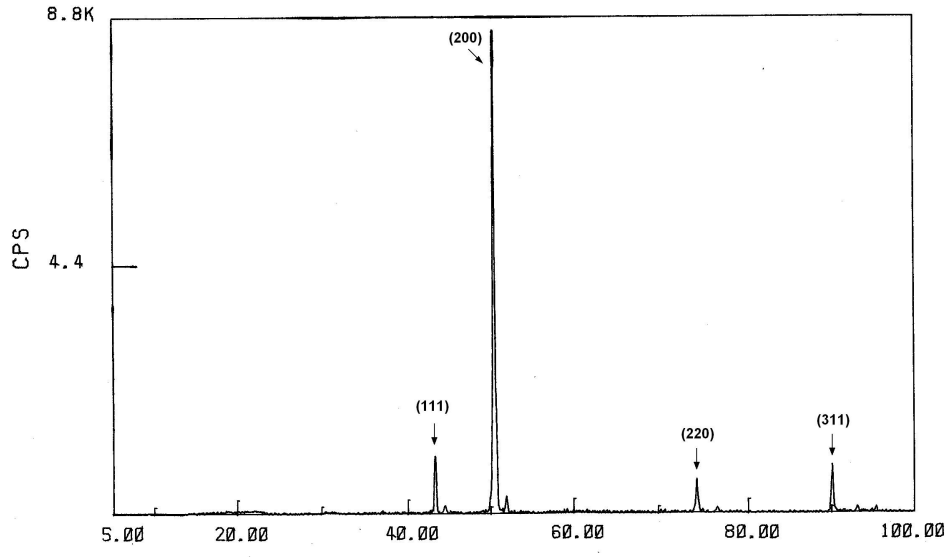

Figure 6. X-ray diffractogram of copper nanowires deposited in membrane having pore diameter of 800nm. (After ultraviolet exposure)

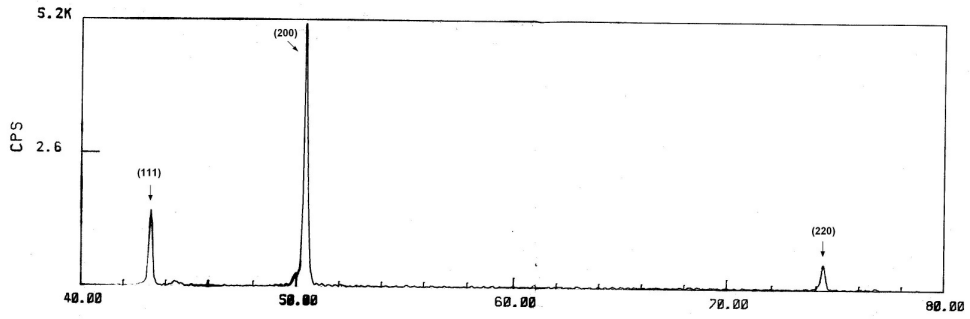

Figure 7. X-ray diffractogram of copper nanowires deposited in membrane having pore diameter of 15nm. (After ultraviolet exposure)

The diffractograms indicate a reduction in texturing of fabricated nanowires following exposure to ultraviolet radiation. The texture coefficients pertaining to each of the diffractograms presented above has been analysed for pole density (P_{hkl}) using the relationship given below [13]:

$$P_{hkl} = \frac{I_{hkl}}{I_{0\ hkl}} \left[\frac{1}{n} \sum \frac{I_{hkl}}{I_{0\ hkl}} \right]^{-1}$$

Where P_{hkl} is the texture coefficient of the plane specified by Miller Indices (hkl); while I_{hkl} and $I_{0\ hkl}$ are the specimen and standard intensities respectively for the given peak and n refers to the total number of diffraction peaks being taken into consideration. The observations pertaining to texture coefficients exhibited by fresh and ultraviolet irradiated specimens are summarized in Table 2.

Table 2: Texture coefficients of Cu nanowires before and after exposure to ultraviolet radiation

State:	**Before UV exposure**		**After UV exposure**	
Pore-size:	**800 nm**	**15 nm**	**800 nm**	**15 nm**
hkl	**Texture Coefficient**			
(111)	0.035	0.031	0.205	0.488
(200)	2.916	2.936	2.518	1.997
(220)	0.049	0.033	0.276	0.516
Std. Deviation	**1.658**	**1.677**	**1.315**	**0.863**

The data presented reveals considerable reduction in texturing for both the specimens upon exposure to ultraviolet radiation, as confirmed by corresponding values of standard deviation. The observed changes in peak intensities are more than the general inherent variability on the order of 2 percent for the powder X-ray diffraction technique [14]. Such a modification in crystal structure of polycrystalline metals is known to require accumulation of a considerable amount of energy and would normally occur during heat-treatment or extensive mechanical straining of the material [15,16].

The observed phenomenon can be explained on the basis of dynamics of ultrafast melting of metals under the influence of high intensity pulsed radiation. The quasi-free conduction-band electrons in metals play a leading role in absorption of electromagnetic radiation incident on the metal surface. The absorption of photon by a lattice electron, followed by an increase in kinetic energy of the latter is known as inverse Bremsstrahlung [17]. The electrons form an expanding plasma as the laser pulses propagate into the metal surface. The intensity of radiation employed in the present work lies well within the linear resonance absorption range, which extends up to 10^{16} W/cm^2 [18]. The typical ranges for electron collision frequency (γ) and plasma frequency (ω_p) for metals are generally taken to be 10^{13}-10^{14} Hz and 10^{15}-10^{16} Hz respectively, while the wavelength of ultraviolet radiation corresponds to a frequency of $\omega = 8.9\text{x}10^{14}$ Hz, which corresponds to the case of large absorption, as $\gamma < \omega < \omega_p$ [19]. The absorbed energy is subsequently converted into heat through electron-phonon interactions [20]. The high intensity of laser beam, coupled with its pulse duration of a few nanoseconds can cause localized heating to above melting point, thereby leading to partial re-crystallization [13,21], which in turn serves to reduce anisotropy of the material and is therefore, thought to be responsible for the observed reduction in texturing.

3. CONCLUSIONS

Nanowires of copper were deposited successfully into the nanopores of Nuclepore polycarbonate membranes having pore diameters of 800nm and 15nm. All the specimens prepared at room temperature (30°C) exhibited a strong texturing for (200) plane, which got reduced considerably upon exposure to pulsed ultraviolet radiation. The observed reduction in texturing is attributed to be due to localized, ultrafast melting and recrystallization.

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