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Improved Optical Scattering in Multilayer Nanowires as Compared to Single Layer Nanowires

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Abstract: Metallic nanowires (Cu, Co, Ni, Cu-Ni, and Cu-Co) have been synthesized by electrochemical deposition using anodic alumina membrane as template. Three electrodes electrochemical cell is used for deposition. The structural and morphological analysis of the synthesized nanowires is done through X-ray diffraction and scanning electron microscopy respectively. The optical absorption spectra have been studied in the wavelength range of 200-700 nm. It has been observed that the multilayer nanowires show more emission for a given input fluence as compared to monolayer metallic nanowires.
Keywords: Electrodeposition, Nanowires, Optical absorption.

Introduction

Metals nanostructures like nanowires possessing one dimension are finding immense scope for high-performance devices like ultrahigh-density magnetic recording, ultrafast optical switching, and microwave devices[1,2]. This is because the surface to volume ratios of nanowires is very high which has resulted into improved performances of the devices[3,4,5]. The shape anisotropy of nanowires imparts considerable variation in physical properties that can be exploited for sensor, logic and memory functions, etc[6,7]. So, non linear optical effects of nanowires are of great importance in some of the above said applications[8]. The optical limiter shows the transmission as a function of fluence. The output fluence is proportional to the input fluence at low input fluence, and as the input fluence become greater than the limiting threshold then output fluence become constant. The strong limiting has been observed in carbon nanostructures. C_{60}[9], carbon nanotubes[10,11] and carbon black suspension[12] are also shows optical limiting behavior. Semiconductor doped glasses[13] and semiconductor nanoparticles[14,15] also exhibit the optical limiting. Metal nanowires also show the optical limiting but there is not much work done in this field. The optical limiting of the nanowires is function of the input fluence as well as wavelength[8]. So, the output fluence depends upon input fluence when wavelength is fixed and on the wavelength range when input fluence is kept constant. The optical limiting properties of nanowires may result into the fabrication of optical limiters with low cost and more efficiency[8]. In this work, single and multilayer nanowires are synthesized and their optical properties are studied by varying the wavelength in UV-visible region keeping input fluence constant.

Experimental

Electrochemical synthesis technique was implemented for the fabrication of Cu, Co, Ni, Cu-Ni and Cu-Co nanowires. Uniform pore size anodic alumina membranes (AAM) of 100 nm diameter and 60 µm length were used as template for synthesis of nanowires. The morphology and crystal structure of the nanowires was studied using electron scanning microscopy (SEM) (JEOL, JSM-6510L) and X-ray diffraction (XRD) (Panalytical X' pert). $Cu.SO_4.5H_2O$ (200 g/l) was used with pH value of 1.8 for Cu nanowires Similarly, Co, Ni, Cu-Co multilayer and Cu-Ni multilayer nanowires were grown using corresponding sulphate as electrolyte. Distilled water is used for preparation of electrolyte. Total five nanowires samples were prepared. For optical measurements, first all the samples were dipped in acetone to remove silver coating and then they all are dipped in NaOH followed by cleaning with distilled water to completely liberate the nanowires from AAM. The optical absorption spectra of all single and multilayer nanowires suspended in ethylene glycol were measured in UV-visible region between 200 and 700 nm using Perkin Elmer spectrophotometer. The nanowires suspended in ethylene glycol were put in the quartz cuvette and then were placed in the cell of spectrophotometer.

Results and Discussion

SEM and XRD characterization has already been done and published before carrying out the optical characterization[3,4,16,17]. So the results of these characterizations are presented here as such. Figure 1 shows the XRD pattern of nanowires. For Cu nanowires, (111), (200) and (220) were the planes corresponds to which three reflection peaks were obtained as shown in Figure1 (a) and can be completely indexed to the Cu face-centered cubic crystal structure [JCPDS card (4-783)]. Some reflection peaks of silver (200) and (220) are also observed. This may be because some remains of silver paste at the bottom of the AAM template. Three specific reflection peaks (100), (002) and (110) were obtained for Co as shown in Figure 1 (b). The reflection peaks in XRD pattern of Co corresponds to hexagonal close packed (hcp) structure of cobalt nanowires. The absence of (101) peak and large magnitude of (002) peak together confirms that the c-axis of the grains within the wires is aligned parallel to the axes of the wires. Some peaks due to AAM were also observed. Figure 1 (c) shows the XRD pattern for Ni consisting of three reflection peaks (111), (200) and (220) and XRD pattern of Cu-Ni multilayer nanowires (Figure 1(d)) shows the presence of the three reflection peaks attributed to planes, (111), (200), (220) at different angles for Cu as well as Ni, confirming the face centered cubic crystal structure for both Cu and Ni. The intensity of reflection peaks observed for Ni in XRD pattern of Cu-Ni multilayer nanowires is lower than that of the reflection peaks corresponding to Cu, confirms more wt% of Cu than Ni. Figure 1(e) shows the three reflection peaks of Cu corresponding to (111), (200) and (220) planes obtained at different angles for Cu X-ray diffraction (XRD) analysis of the Co–Cu multilayer nanowires embedded in AAO template and two reflection peaks corresponding to Co were along (111) and (200) plane. This confirms the face centered cubic crystal structure for both Cu and Co. The peaks corresponding to AAM is also observed.

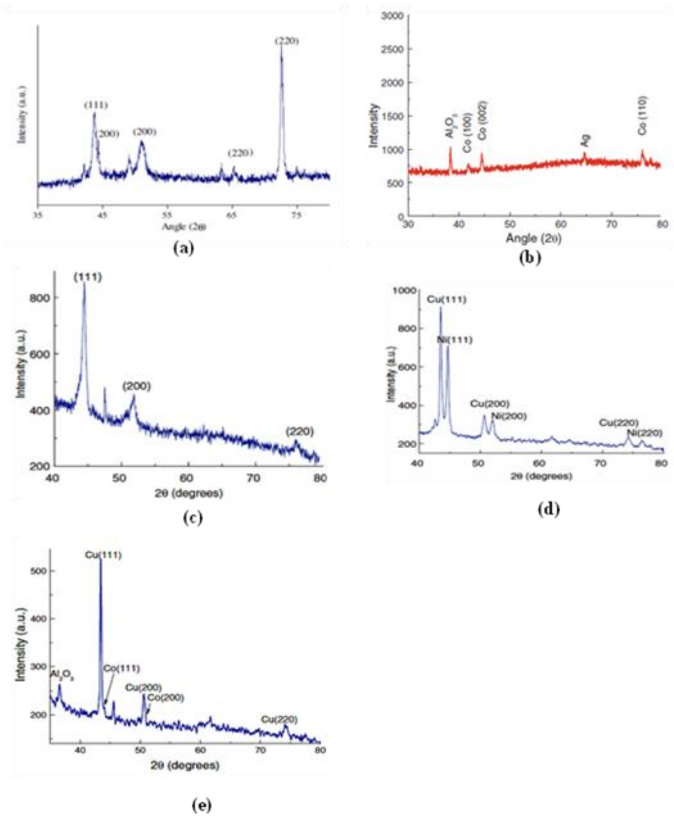
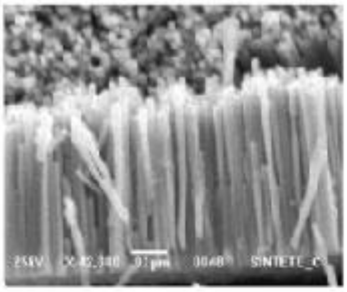
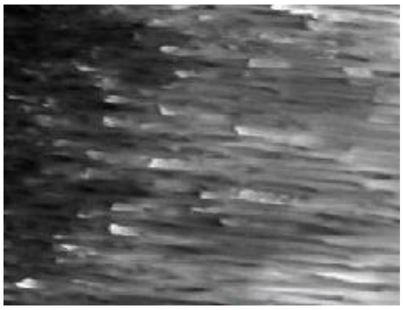


Figure 1 XRD patteren of synthesised nanowire (a) Cu nanowires (b) Co nanowires (c) Ni nanowires (d) Cu-Ni nanowires (e) Cu-Co nanowires

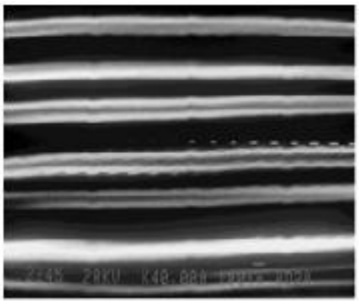
Figure 2 (a), (b), (c), (d) and (e) shows the SEM for Cu, Co, Ni, Cu-Ni and Cu-Co nanowires. It is clear from the SEM of Figure 2 that the growth of nanowires is dense and uniform. There are some dark and bright fringes in multilayer nanowires as shown in Figure 2(e). These dark and bright fringes show the deposition of two different materials. Bright corresponds to one metal and dark corresponds to the second metal. There are no such fringes in metallic nanowires of single metals.



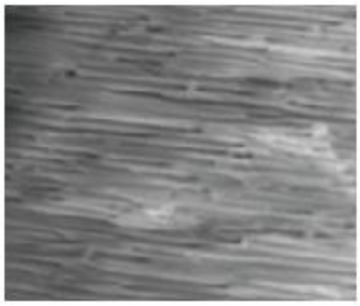
(a) SEM for Cu nanowires



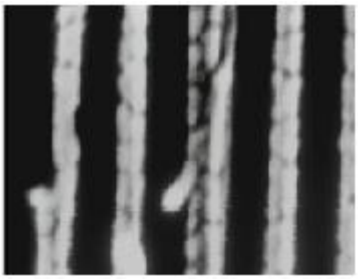
(b) SEM for Co nanowires



(c) SEM for Ni nanowires



(d) SEM for Cu-Ni nanowires



(e) SEM for Cu-Co nanowires

Figure 2 SEM micrograph of synthesized nanowires

On clearly analyzing the Figure 2(e), it is observed that the width of the bright fringe is more as compared to the dark fringe. So, it leads to the conclusion that during the electrochemical deposition of multilayer nanowires, one material deposited in large amount as compared to the other material. The wt% of one metal is more as compared to other metal. The noble nature of the metal decides the more or less deposition of the metals. More noble metal will deposit more as compared to the less noble metal. The optical absorption spectra of all samples are shown in Figure 3 below.

From Figure 3 absorption bands are observed in the wavelength range from 300 nm to 375 nm. One more absorption dip is noticed in case of copper nanowires around 450 nm. The first dip corresponds to the photo induced bulk-plasmon emission[18]. The absorption dip at 450 nm corresponds to the surface Plasmon resonance[19]. The interband d-sp transition may be the reason for further gradual decrease in absorption It has been observed from Figure 3 that the Cu and Ni nanowires are having good optical scattering and Ni is having highest optical scattering among all three mentioned single layer metallic nanowires but optical scattering of Co is weak in the range 375 nm to 700 nm. The multilayer nanowires of Cu-Co and Cu-Ni are showing good optical scattering in comparison to the Cu and Co metallic nanowires. The presence of Ni in Cu-Ni multilayer nanowires has enhanced the optical scattering of Cu-Ni nanowires .It is observed that multilayer nanowires showing better optical limiting behavior as compared to single metallic nanowires. The presence of dip towards lower wavelength side in absorption spectra of multilayer nanowires confirms that the absorption in the multilayer nanowires corresponds to the photo induced bulk-plasmon emission.

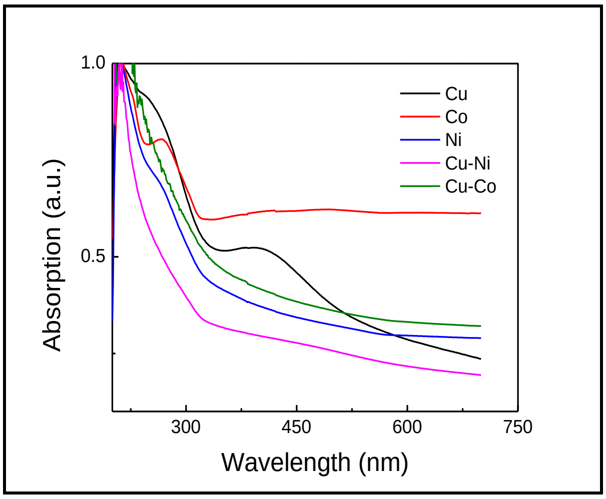


Figure 3 Optical absorption spectra of nanowires

Conclusion

Synthesis of Cu, Co, Ni, Cu-Co and Cu-Ni metallic nanowires have been done using three electrodes electrochemical cell. AAM of uniform pore size is used as template. Crystal structures of the all five samples of nanowires have been analyzed by XRD. SEM clearly shows the uniform and dense growth of nanowires. Perkin Elmer spectrophotometer was used to obtain the optical absorption spectra for all the samples of nanowires. The absorption spectrum of Cu nanowires shows the photo induced bulk-plasmon emission and surface plasmon resonance. It is concluded that the optical scattering is more in multilayer nanowires as compared to metallic nanowires of single material.

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