Optical limiting properties of metal nanowires

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Metal (Cu, Co, Ni, Pd, Pt, and Ag) nanowires (MNWs) have been produced using anodic aluminum oxide as template. The grown MNWs are characterized by scanning electron microscopy, x-ray diffraction, transmission electron microscopy, and electron diffraction. The optical limiting properties of the MNWs are also studied and results obtained at 532 and 1064 nm indicate that MNWs have broadband optical limiting capability and the optical limiting performances of some MNWs are comparable to or better than that of carbon nanotubes. It was found that the nonlinear response of MNWs is dominated by nonlinear scattering. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2208549]

One-dimensional nanostructured metals have attracted great attention because of their potential applications in ultrahigh-density magnetic recording, ultrafast optical switching, and microwave devices.[1,2] In many of these applications, nonlinear optical effects may play an important role. An optical limiter exhibits the following transmission behavior, which is a function of the fluence. That is, the output fluence is proportional to the input fluence at low input fluence but approaches a constant after the input fluence becomes greater than the limiting threshold. Recently, strong optical limiting effects were observed in carbon nanostructures, including C_{60},[3,4] carbon nanotubes,[5–7] and carbon black suspension (CBS).[8,9] Semiconductor-doped glasses[10,11] and semiconductor nanoparticle solutions[12–14] have also been investigated for the nonlinear optical applications. On the other hand, metal nanowires (MNWs) have been grown and their applications in high-density storage devices have been explored.[15,16] However, to the best of our knowledge, the optical limiting property of the MNWs has not been studied. Besides the scientific interest in mechanisms of nonlinear optical properties in such nanosystems, study of optical limiting properties of the MNWs may lead to cheap and efficient optical limiters. In this work, the nonlinear optical properties of the MNWs are studied and their potential applications as optical limiters are explored.

Uniform-sized MNWs, i.e., Cu, Co, Ni, Pd, Pt, and Ag nanowires, were produced by electrochemically depositing the metal into the anodic aluminum oxide (AAO) template that had the uniform pore structures. The morphology and crystalline structure of the deposited MNWs were studied by scanning electron microscopy (SEM) (JEOL JSM-6700F) and x-ray diffraction (XRD) (Brucker AXS D8). The optical absorption spectra of the MNWs suspended in water and contained by 1-cm-thick quartz cells were measured in the UV-visible region between 200 and 1100 nm on Shimadzu UV2101. The optical limiting properties of the MNWs suspended in water and contained by 1-cm-thick quartz cells were studied by fluence-dependent transmission measurements, using 7-ns light pulses generated from a frequency-doubled Q-switched Nd:YAG (yttrium aluminum garnet) laser (Spectra Physics DCR3), at two different wavelengths (532 and 1064 nm). The laser pulses were produced at 10 Hz repetition rate and were focused on the central point of the quartz cell with a spot radius of 30 μm. The nonlinear scattering measurements were conducted with the detector set at various angles from the propagation axis of the transmitted laser pulses. An aperture was placed in front of the detector. The radius of the aperture was adjusted so that a solid angle for collecting the scattered light was 0.015 rad.

All the MNWs tested were grown from identical AAO template which was prepared following the modified two-step anodization.[15] Briefly, the pure Al sheet (99.999%) was anodized at 40 V in an oxalic acid solution of 3 wt % at room temperature. After removing the alumina, the ordered pore arrangement was achieved during the second anodization. dc electrodeposition was performed at an applied voltage of 1.5 V and the temperature of 25 °C. For Ni nanowire deposition, 240 g/l $NiSO_4 \cdot 7H_2O$ with the pH value of 2.5 was used. Other metal nanowires were prepared at the same electrodeposition conditions as the Ni deposition, using a corresponding sulfate or chloride electrolyte. A total of six MNW samples were prepared and studied, which are Ni nanowires (NiNWs), Pd nanowires (PdNWs), Pt nanowires (PtNWs), Ag nanowires (AgNWs), Cu nanowires (CuNWs), and Co nanowires (CoNWs). For optical measurements, the MNWs were totally liberated from AAO template (using 1M NaOH solution), cleaned in distilled water till pH=7, and suspended in distilled water. All six samples have similar diameter and length because of identical AAO template and deposition conditions.

Figure 1 shows the SEM image of a typical MNW sample embedded in AAO template. The AAO template was partly removed so that the embedded MNWs become observable. The diameter and length of nanowires are approximately 50 nm and 30 μm, respectively. Figure 2(a) displays the XRD patterns of the MNWs. The Ni, Co, and Ag nanowires each exhibits only one diffraction peak at the orientation along [220], [100], and [220], respectively. For Pd, Pt, and Cu nanowires, the characteristic peaks are observable in their XRD patterns. The high intensity and small peak width indicate good crystallinity of the nanowires.

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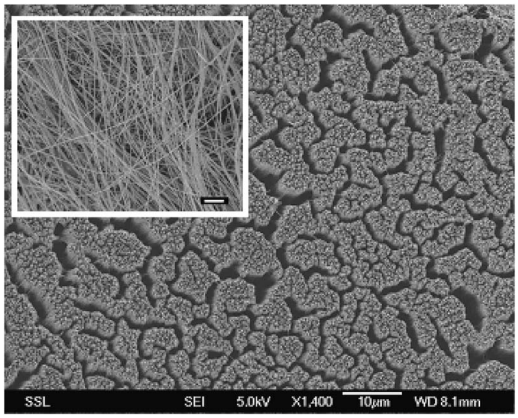

FIG. 1. The SEM images of MNWs grown on AAO template with the alumina matrix partially removed. The inset shows the MNWs after the AAO was totally removed. The scale bar in the inset is 1 μm.

In the optical absorption spectra shown in Fig. 2(b), absorption bands around 250–600 nm are noticed, particularly for Co, Cu, and Ag nanowires. There is a dip at 320 nm (3.8 eV) in the absorption spectrum for Ag nanowire solution. According to Boyd *et al.*,[17] this is photon-induced Ag-bulk-plasmon emission. The broadband of the absorption around 430 nm (2.9 eV) in the Ag spectrum is therefore attributed to surface plasmon resonance[18] and its long-wavelength tail is due to *d-sp* interband transitions.[17] Similar assignments can be applied to the absorption bands for Cu and Co nanowires.[18] The optical absorption is weak for Ni, Pd, and Pt nanowire solutions in the entire range between 300 and 1100 nm. It seems that the latter group of metals has higher values of work function and first ionization potential[19] and their plasmon resonance would be in the shorter wavelength range.[20]

To study the nonlinear optical (NLO) response of the MNWs, the fluence-dependent light transmission measurements were conducted on the six samples under the same conditions at two wavelengths, 532 nm [see Fig. 3(a)] and 1064 nm [see Fig. 3(b)], respectively. Nevertheless the concentration of the MNWs in the tested solutions could be different, adjusted in such a way that their linear transmittances are all 80%. In Fig. 3(a) the energy transmittance at the light fluences less than 0.1 J/cm^2 is constant for all the samples. However, in excess of 0.1 J/cm^2, the transmittance

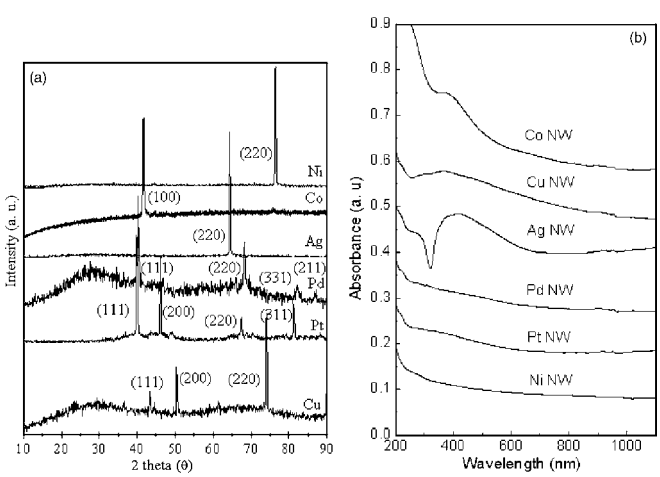

FIG. 2. (a) The XRD patterns of the MNWs and (b) the optical absorption spectra of the MNWs.

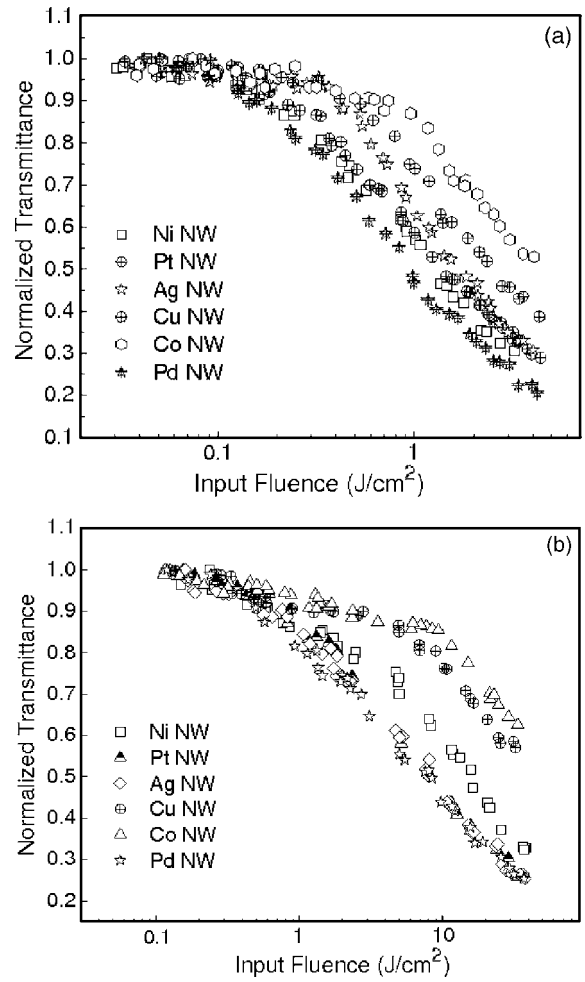

FIG. 3. The optical limiting response of the MNWs measured with 7-ns laser pulses at (a) 532 nm and (b) 1064 nm wavelengths.

decreases as the incident fluence increases, a typical limiting property for all nanowires. The limiting threshold, defined as the incident fluence at which the transmittance falls to 50% of the normalized linear transmittance,[5] is different for different samples. The limiting threshold at 532 nm is 0.9, 1.2, 1.3, 1.7, 2.5, and 4.2 J/cm^2 for Pd, Ni, Pt, Ag, Cu, and Co nanowires, respectively. The nonlinear optical limiting responses of Pd, Ni, Pt, and Ag nanowires are comparable to or slightly better than those of single-wall and multiwall carbon nanotubes[6,21] (MWCNTs) (Table I), whereas CuNWs and CoNWs are slightly poorer. Figure 3(b) shows similar optical limiting properties of MNWs at 1064 nm. The optical limiting of Pd, Pt, Ni, and Ag nanowires is better than or comparable to those of carbon nanotubes at 1064 nm, whereas Cu

TABLE I. The limiting threshold of the MNWs at 532 and 1064 nm. The limiting threshold of MWCNT is also listed for comparison.

Samples	F_{th} at 532 nm (J/cm^2)	F_{th} at 1064 nm (J/cm^2)
PdNW	0.9	8
NiNW	1.2	8
PtNW	1.3	8
AgNW	1.7	10.8
CuNW	2.5	>30
CoNW	4.2	>30
MWCNT	1.0[a]	10.0[a]

[a]Reference 19.

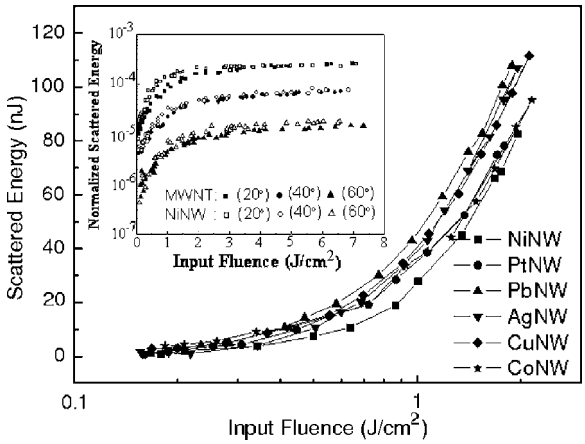

FIG. 4. Nonlinear scattering measured with 532-nm, 7-ns laser pulses at a forward angle of 10° with a solid angle of 0.015 rad. The inset shows the scattered energy of the NiNW and the MWCNT as a function of the input fluence at various forward angles.

and Co nanowires are slightly poorer. The limiting threshold at 1064 nm radiation is 8, 8, 8, and 10.8 J/cm^2 for Pd, Ni, Pt, and Ag nanowires and larger than 30 J/cm^2 for Cu and Co nanowires, respectively. Obviously the nonlinear optical limiting is much weaker at 1064 nm as compared to that at 532 nm.

There are several mechanisms proposed for optical limiting, including two-photon absorption (TPA), free-carrier absorption (FCA) associated with TPA, reverse-saturable absorption (RSA), self-focusing/defocusing, thermal blooming, and nonlinear scattering.[22,23] The observation of nonlinear limiting for all the MNWs at 1064 nm laser incidence in this work shows that nonlinear scattering is a major mechanism responsible for the nonlinear limiting of the MNWs, since the energy of 1064 nm laser light is too low (1.16 eV) for single-photon excitation which generally requires much higher photon energy (e.g., 2.15 eV for Cu and 3.6 eV for Ag).[17] In nonlinear scattering, the key mechanism is the photon-induced ionization and excitation of the metal atoms in MNW suspensions. This leads to the formation of rapidly expanding microplasmas, which strongly scatter the incident light and results in the limiting behavior.[6,21] The response of the optical limiting induced by the nonlinear scattering is related to the ability of the photoionization of the atoms and the subsequent expansion of the microplasmas, as previously observed in different carbon nanotubes.[6,21] Since for all the MNWs in this work with 1064 nm laser the ionization must be a two-photon or multiple-photon process, the light scattering by these samples is nonlinear, rapidly increasing with increasing light intensity.[23,24] Moreover, the nonlinear scattering, measured at 532 nm for all the MNWs, becomes stronger with increasing incident energy. One of these measurements at an angle of 10° is displayed in Fig. 4. The nonlinear scattering is confined in the forward direction, and the scattered light energy decreases as the scattered angle arises, as shown in the inset of Fig. 4. Similarity in nonlinear scattering between the MNWs and MWCNT strongly indicates that nonlinear scattering is dominant for the optical limiting observed in the MNWs. On the other hand, Pd and Pt are expected to have optical absorption only at shorter wavelengths (<200 nm) due to higher surface plasmon resonance and their nonlinear limiting is more evident, slightly better than carbon nanotubes. For the nonlinear limiting of MNWs at 532 nm (2.32 eV) laser incidence, some *d-sp* interband or near-Fermi-level intraband transitions may become possible and other mechanisms than nonlinear scattering may also contribute to the nonlinear limiting. Nevertheless the fact that MNW samples have similar trend of the variation in optical limiting response in the two laser energies (532 and 1064 nm) appears to indicate that nonlinear scattering is the dominant mechanism.

In summary, we have grown high-quality MNWs, including Ni, Co, Cu, Pt, Pd, and Ag nanowires, using AAO template. XRD patterns illustrated that the Ni, Co, and Ag nanowires are single crystals while Pt, Pd, and Cu nanowires are polycrystalline. The optical limiting properties of Pt, Ni, Pd, and Ag nanowires are better than those of Cu and Co nanowires. With the observation of optical limiting both at 532 and 1064 nm, nonlinear scattering is believed to make a dominant contribution to the limiting performance of MNWs.

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