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RAMAN STUDY OF INTERFACIAL INTERACTIONS IN CARBON NANOTUBES(CNTs)-CeO_2-Al_2O_3 INTEGRATED SYSTEM

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ABSTRACT. Multiwalled carbon nanotubes (MWCNTs) were deposited from solution phase onto the nanostructured CeO_2 film. New interfacial CNTs-CeO_2 interactions were identified by Micro-Raman technique. Results show that the typical Raman signal of CNTs is modulated by the surface morphology. As a result of the CNTs-CeO_2 interactions the G-peak of CNTs is split into two peaks. Different shift of G-peaks is detected when depositing CNTs onto CeO_2 films having different morphologies.

Keywords: Carbon nanotube, CeO_2, combinatorial materials, Raman, split, shift.

INTRODUCTION

Carbon nanotubes are a sort of attracting nanomaterials which has attracted wide interest in many areas of science and technology since 1991 [1,2]. The combination of CNTs with nanocrystals is expected to be useful for applications in catalysts, sensors or nanoelectronic devices [3] mainly because its optical and electronic properties are affected by the interface between the CNT and other materials. Several studies showed that deformation of nanotubes adsorbed on different substrate may occur [4]. Since the significant dependence of the electronic structure of CNTs on the conformation, this phenomenon offers a new method for appropriate justification of the optoelectronic properties of CNTs towards application requirements by controlling the surface morphology of the substrate.

As a very useful kind of wide-band-gap semiconductor, CeO_2 has been extensively investigated not only because of its excellent biocompatibility, non-toxicity, high chemical stability, transmission in the visible and infrared regions, efficiency for absorbing ultraviolet radiation, but also since it is a key component of the catalyst used for eliminating contaminants in automobile exhaust gases [5-7].

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According to the advantages of CNTs-CeO_2 system mentioned above great effort has been performed to coat CNTs with CeO_2 nanoparticles [8-10], namely using CNTs as supporters. In contrast, only few studies focus on the other possibility: utilizing CeO_2 film as substrate to deposit CNTs on its surface. Preparation of the CNTs-CeO_2 combinatorial material on this way may offer stronger interfacial interactions and can result in a possible large deformation of CNTs.

Here we report deposition of CNTs onto the self-assembled CeO_2 films formed on Al_2O_3 substrates [11]. The new interface formed between the later two surfaces was investigated by micro-Raman method. The splitting of the G-peak of CNT was investigated as the function of the surface morphology of the substrate.

RESULTS AND DISCUSSION

The functionalized MWCNT-OH nanotubes were dissolved in methanol solvent and the saturated solutions were then characterized by photoluminescence (PL) spectrofluorometer (Jobin-Yvon/SPEX). Using 337 nm excitation wavelength, emission peak were detected at about 442 nm. This peak reflects presence of CNTs in the methanol solutions. This PL setup was then used to identify the carbon nanotubes adsorbed on the CeO_2 surfaces. In the case of low surface coverage, no fluorescence signal could be detected by illumination of large surface area. This property probably due to the strong scattered light originated from the substrate region uncovered by the nanotube.

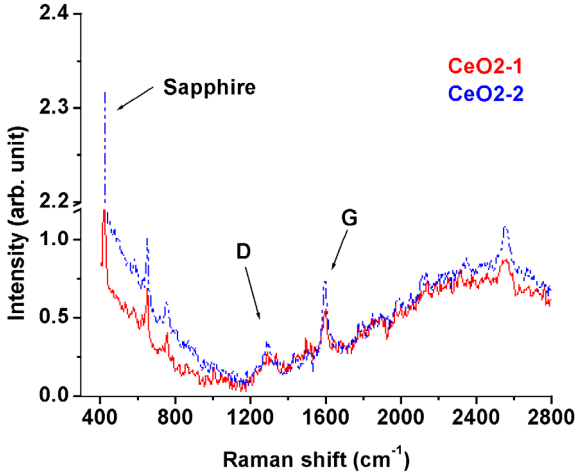

Figure 1. Raman spectra of CNT layer deposited onto the different CeO_2 substrate measured by the conventional method. The typical peaks of CNTs, *G-, D-* and also the typical peak of sapphire were indicated by arrows.

Conventional Raman measurement ended with same conclusion (see Figure 1): The *G*-peak of CNTs can only be observed, when the *D*-peak nearly submerged into the background. Considering the applicability of the confocal optical setup for direct investigation of the new CNT-CeO_2 interface we applied micro-Raman technique for further studies. In this case the *D*- and *G*-peaks of CNTs can be observed clearly when the detection area and the excitation laser beam was exactly focused onto the sparsely distributed black spots (Fig.2). The *G*- and *D*-peaks are attributed to the *C-C* sp^2 interaction (E_{2g}) and the structural disorder in the graphite-like material, respectively [12,13]. At the same time two new peaks around 1400cm^{-1} were observed. It is obvious to attribute these two peaks to the new interactions presented between Al_2O_3 and CeO_2 nanostructures since the following reasons: these peaks at about 1400cm^{-1} are not observed for the individual Al_2O_3 or CeO_2 crystals. Previous studies showed that most of the characteristic peaks of these materials are located within the 200 cm^{-1} -1000cm^{-1} range. Furthermore, supposing that such peaks came from Al_2O_3 or CeO_2, they should appear in one Raman spectra together with other typical peaks. However, in fact on one hand, in conventional Raman spectra the typical sharp peak of Al_2O_3 appears at 418cm^{-1} while nothing observed at 1400cm^{-1}. The peaks at 1400cm^{-1} only dominate in the absence of the Raman active mode of CeO_2 (F_{2g} peak) at 464 cm^{-1}. Mention, the mentioned new peaks are not typical peaks of CNTs. In addition, these peaks cannot reflect the new interface formed between CNTs and CeO_2. When the *G*- and *D*- peak of CNTs are weakened, they are pronounced, namely they don't appear together with typical peaks of CNTs.

Previous work [14] reported that the *G*-peak of CNTs at about 1580cm^{-1} splits into several peaks when the CNTs are strained, e.g. a tube bends and forms a ring. Now we paid more attention if such new interfacial interactions described above will bring some novel changes to the Raman signal of CNTs. Here we observed two interesting phenomena: i) similarly to the previous results, *G*-peak split into two individual peaks, which strangely discovered in micro Raman only. ii) using two CeO_2 films with different morphologies, the *G*-peaks of CNTs show different Raman shifts by about 9cm^{-1}.

Table 1. Thickness of CeO_2 (t) and corresponding Raman shift

Sample	Thickness *t* (nm)	Typical Raman shift of CNTs (cm^{-1})
CeO_2-1	9.35	1590.4
CeO_2-2	10.18	1581.2

Considering that during conventional Raman measurements never such splitting or shifting of the *G*-peaks of CNTs was detected we can only associate these properties to the interfacial effect between Al_2O_3 substrate and CeO_2 nanostructures. The CNTs adsorbed on the nanostructured CeO_2 surface are very close to such interface and under strain the *G*-peak will split into two individual peaks. On two CeO_2 films which have slightly different

thickness, the *G*-peak showed a 9cm^{-1} shift. If keeping in mind that the changes of CNTs are owing to the interfacial effect, it will be easy to understand this small difference between the Raman shifts. If we increase the mean grain size of CeO_2 islands, the detected interfacial interactions, namely the intensity of Raman peaks will decrease and finally disappear while the F_{2g} peak located at 460cm^{-1} and which is typical for CeO_2 crystal will gradually arise. Figure 2 and 3 together with Table 1 clearly show decreased Raman intensity at increased thickness of CeO_2. The *G*-peak also shows different shifts on these two substrates. Indeed, the interfacial interaction are very sensitive to the thickness especially in nanoscale and results in different deformation of CNTs. Finally it shows a shift and splitting of *G*-peak, indicating the in-plane symmetric *C*–*C* stretching.

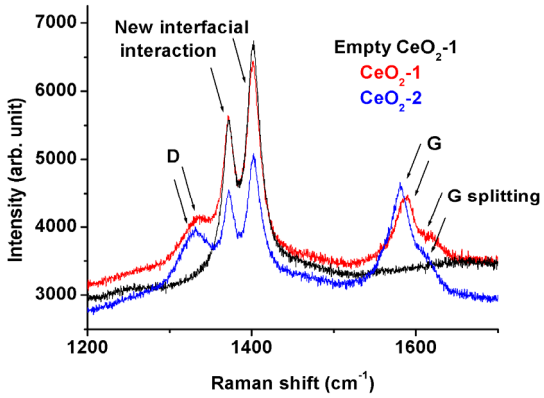

Figure 2. Micro-Raman spectra of CNT layers deposited onto the different CeO_2 substrates. The typical peaks of CNTs, *G*- and *D*- , the splitting of *G*-peaks and also the two typical peaks of the new interfacial interactions were indicated by arrows.

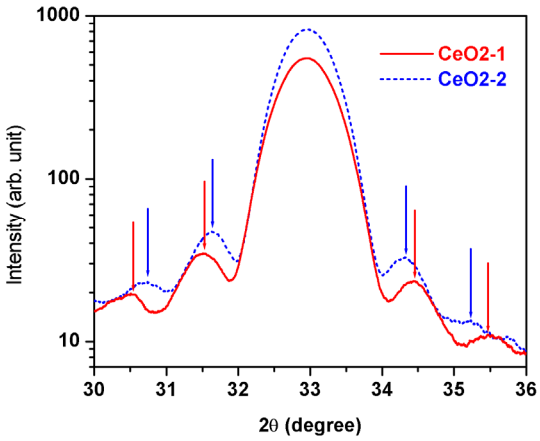

Figure 3. Typical XRD patterns of CeO_2 films. The most intense peaks are CeO_2 (002). Laue oscillations were indicated by arrows.

CONCLUSIONS

CNT layers were deposited onto the nanostructured CeO_2 surfaces originally grown on sapphire substrate. These combinatorial materials were investigated by Raman spectroscopy. Results reflect that the Raman signal of the CNTs is affected by the interactions presented within the CeO_2-Al_2O_3 interface. Furthermore, the split of the *G*-peak of CNTs highly depends on the thickness of the CeO_2 film. Since the morphology of CeO_2 is easily controllable by the growth conditions, the optoelectronic properties of the CNTs can be tuned towards the application requirements.

EXPERIMENTAL SECTION

All the CeO_2 films were grown by pulsed laser deposition technique and were then annealed at high temperature (1025°C) to form self-assembled nanostructures as described earlier [11]. Before CNTs deposition XRD was routinely employed to measure the thickness of CeO_2 film [15]. The deposition method of CNTs is liquid phase epitaxy (LPE). Hydroxylated multiwalled CNTs (MWCNT-OH) powder was first dissolved by MeOH forming MWCNT-OH saturated solution. This solution was dropped onto nanostructured CeO_2 films. The raw MWCNTs are 8-10 nm in diameter and 5-15 μm in length with the purity of more than 95%. Volume of the deposited CNTs can be controlled by using different number of drops. During evaporation of MeOH, the CNTs adsorbed onto the CeO_2 surface. In details, 20 drops for each sample, each drop 10 μl, the interval between two drops is 25 min.

Conventional Raman spectra were recorded by Nicolet NXR 5700 FT–IR–Raman (UNICAM) photometer. Micro-Raman investigations of the samples were measured using a LabRam 600 spectrometer from Jobin-Yvon. The optimal confocal spatial and depth resolution is down to 1μm. The sample surface was illuminated with 632.8 nm monochromatic light with less than 10 mW/cm^2 power density.

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[15] The thickness of CeO_2 films was determined by the XRD Laue oscillations using $t = \frac{\lambda}{2[\sin(\theta_i) - \sin(\theta_{i-1})]}$, where θ_i and θ_{i-1} are the positions of adjacent satellites.