Hong-Ou-Mandel quantum effect on “polymer - multiwall CNT” composites

Liudmyla A. Karachevtseva[1], Mykola T. Kartel[2], Oleg O. Lytvynenko[1], Yurii I. Sementsov[2]

[1] V. Lashkaryov Institute of Semiconductor Physics, NASU, Prsp. Nauki, 41, Kiev-03028, Ukraine.
[2] O. Chuiko Institute of Surface Chemistry, NASU, 17 General Naymov Street, Kyiv 03164 Ukraine.
lytvole@gmail.com

Introduction

Earlier we analyzed high-resolution IR absorption spectra of macroporous silicon to investigate phonon-polaritons resulted in detection of dipole-active transverse optical (TO) vibrations, photon beam splitting and giant two-polar absorption oscillations with high amplitudes of $\pm10^7$ arb.un. The generated photoelectrons link heavily with holes in the macropore potential pits forming 2D interference polaritons at room temperature. 2D polariton transforms into 1D polariton according to secant law in spectral area of TO-vibrations of Si-Si-bonds and P_b centers in macroporous silicon. Surface polaritons interact with photons strongly due to resonances of dipole-active vibrations and surface modes at boundaries Si-SiO_2 and SiO_2+PEI-ncCdS on macropores. Shape of oscillations corresponds to the interference of polaritons as the eigenstates of the system nanocoating – silicon matrix – waveguide modes. In our case, the vertically polarized light along macropores (*z* direction) and horizontally polarized light (*x* direction) permit the explanation of results as two-photon interference (the Hong-Ou-Mandel effect). As a result, macropore is a beam splitter (BS) with maximum and minimum coincidences for measurements with parallel and perpendicular polarizations, respectively. We observed constructive interference of the two-photon states corresponding to photons exiting through the same output ports (bosonic behavior). Two-polar resonances in $\pm z$ direction are determined by 1D polaritons (destructive interference of the two-photon states, fermionic behavior). Furthermore, 1D polaritons are perspective for high-coherent optical quantum computers on macroporous silicon with nanocoatings, for lasers and new metamaterials.

Now we analyzed high-resolution IR absorption spectra of “polymer–multiwall carbon nanotubes (CNTs)” composites to investigate phonon-polaritons resulted in detection of dipole-active TO vibrations, photon splitting and two-polar absorption oscillations with amplitudes up to $\pm10^5$ arb. un. and compared with *macroporous silicon structures*.

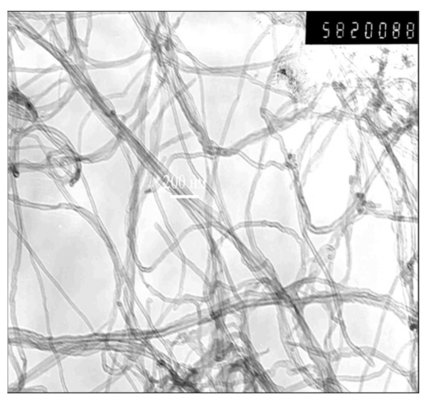

Fig. 1. Group of multiwall carbon nanotubes.

Multiwall CNTs (Fig. 1) are among the most anisotropic materials known and have extremely high values of Young’s modulus. Carbon nanotube aspect ratio of length to diameter is more than 10^3. New composites with CNTs as additives are investigated intensively during the last decade. Composites characterized by extremely high specific strength properties, electrical and thermal conductivity.

Earlier the opportunity to enhance the properties of nanostructured surfaces was investigated on films of “polymer–multiwall CNTs” composites and the composites based on 2D macroporous silicon structures with nanocoatings. Influence of sp^3 hybridization bonds on polymer crystallization and strengthening we evaluated for composites of polypropylene and polyamide with multiwall CNTs. The IR absorption peak dependences on CNT content at frequencies of sp^3 hybridization bonds we described by 1D Gaussian curves for the diffusion equation in the electric field (Fig. 2). Distance between nanotubes in composite depends on the concentration of CNTs (N_{CNT}), its content (% CNT) and the nanotube volume (V_{CNT}). IR absorption maximum for sp^3 bond hybridization (D) of composites corresponds to the average distance a = 0.35 μm between the cylindrical CNT with diameter of 20 nm and a length of 2 μm. The electric field between nanotubes and polymer matrix (Fig. 3) has a thickness w of space charge and is equaled to 0.17 μm for maximum of IR absorption. The electric field intensity between nanotubes and polymer matrix is equal to $6.3\cdot10^3$ V/cm at 0.25 % CNT.

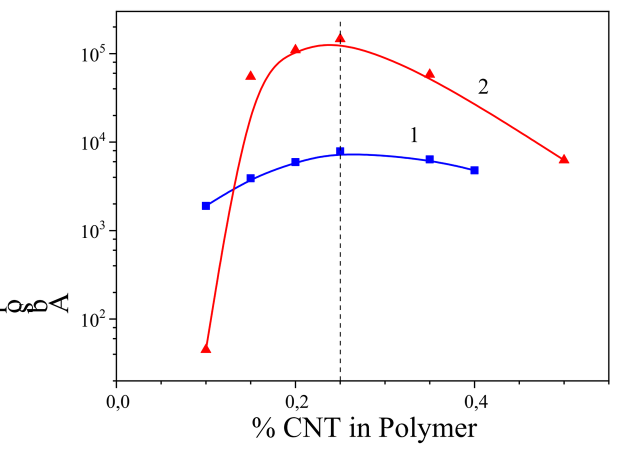

Fig. 2. IR absorption by sp^3 hybridization bonds (D) in composites based on polypropylene (1) and polyamide-6 (2) *vs* CNT content in polymer.

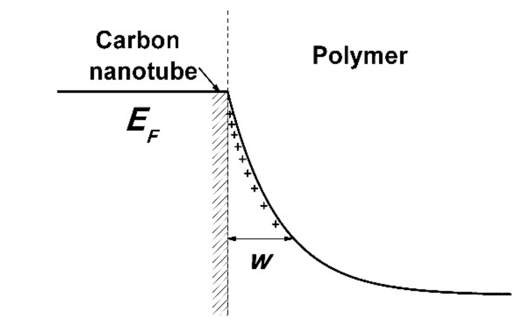

Fig. 3. Band bending and SCR width w at the "polymer-CNTs" boundary.

Procedure and Results

The composites were made of polypropylene, polyamide-6, polyamide-12 and polyvinyl chloride filled by a mixture of CNTs with the polymer powder and dried. Thin polymeric films (100–150 μm thick) without and with CNTs were prepared. We obtained compression and tension tests of the polymeric materials and their composites using tensile machine with the automatic recording of the deformation diagrams. Low concentrations of CNTs resulted in significant increases in Young’s modulus, impact strength and interfacial adhesion.

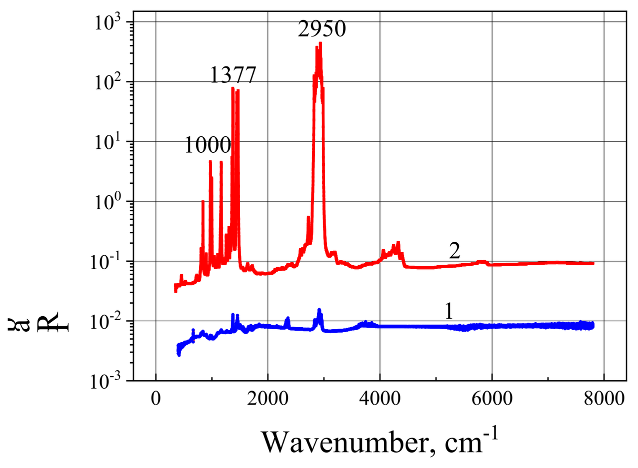

Fig. 4. IR absorption spectra of polypropylene (1) and “polypropylene-CNTs” composite (2).

High-resolution optical absorption spectra we measured in the 200–8500 cm^{-1} spectral range with a resolution of 1 cm^{-1}. We obtained optical absorption spectra at normal incidence of IR radiation on a sample in the air at room temperature. IR absorption of polymer composite films exceeds that of polymer films essentially. According to Fig. 4, IR absorption exceeds the absorption of polypropylene by 10–10^3 times in the entire spectral range measured after adding CNTs to polypropylene (concentration of 0.25 %).

After adding carbon nanotubes to polyamide-12 (PA-12), the IR absorption of composites exceeds the absorption of polymers by 10^3–10^5 times in the entire measured spectral range. IR absorption increases between 1400–1500 cm^{-1} for polyvinyl chloride (PVC) after adding CNTs to polymers. The intensity of vibrations increases for C–C bonds (835 and 1000 cm^{-1}), $\gamma_r(CH_3)$ – 970 cm^{-1}, $\gamma_\omega(CH_3)$ – 1170 cm^{-1}, at the frequency of sp^3 hybridization (D) – 1360 cm^{-1}, as well as oscillations: $\delta(CH_3)$ – 1380 cm^{-1}, $\delta(CH_2)$ – 1440 cm^{-1}, $\delta(CH_3)$ – 1470 cm^{-1}. At the same time, IR absorption increases significantly at frequencies 690 cm^{-1} – Amide V and at a frequency of 1358 cm^{-1}, which corresponds to fluctuations of $\gamma_\omega(CH_2)$ and frequency of sp^3 hybridization (D). Higher C–C fluctuations, CH, CH_2 and CH_3 bond absorption correspond to higher absorption at the frequencies of $\gamma_\omega(CH)$ and $\gamma_\omega(CH_2)$ vibrations. In addition, two-polar IR absorption was measured.

Table 1 shows types of bonds for two-polar IR absorption after adding carbon nanotubes to polymers. Two-polar IR absorptions were measured on polypropylene (PP) composite at 1379 cm^{-1}, on polyamide-6 (PA6) in spectral area $\gamma_\omega(CH_2)$ vibrations, $\delta(CH_3)$ (E) for frequency of sp^3 hybridization bonds –1260 (D) and –2950 (2D); polyamide-12 (PA12) –1358 (D), 1529 (G), 1632, –2904 (2D), and polyvinyl chloride (PVC) –690 cm^{-1}.

In general, two-polar IR absorption bands we measured on all investigated composites with negative IR absorption at spectral positions of sp^3 hybridization bonds and/or double sp^3 hybridization bonds of carbon multiwall nanotubes in polymer composites. A group of peaks 1260–1379 cm^{-1} (Table 1), called “D-band”, is assigned to the presence of disorder in graphitic materials. Thus, the origin of D-band in nanotubes is a level of “disorder” in graphite. D-band is active for nanotubes satisfying a certain chirality due to double resonance conditions. In addition, the D-band of isolated CNTs can be decomposed into two bands; their separation depends upon the incident laser energy. A group of peaks in the 1550–1600 cm^{-1} range constitutes the G-band. In graphite, a single peak is present at 1582 cm^{-1}, corresponded to the tangential vibrations of the carbon atoms.

Double (2D) sp^3 hybridization bonds 2950, 2904, 3240 cm^{-1} (Table 1), are second-order mode of D-band. 2D-band increases in intensity with increase in defects as part of the density of states. 2D-band indicates the long range order in a sample, and arises from a two-phonon secondorder scattering process. It results in creation of inelastic phonons.

Table 1. Types of bonds for IR absorption growth after adding to polymers carbon nanotubes

PP		PA6		PA12		PVC	
Type of bonds	Frequency, cm^{-1}	Type of bonds	Frequency, cm^{-1}	Type of bonds	Frequency, cm^{-1}	Type of bonds	Frequency, cm^{-1}
$\gamma_\omega(CH)$	1377 –1379 (D) –2850, 2950 (2D)	$\gamma_\omega(CH_2)$	1249, –1260 (D), –2950 (2D)	$\gamma_\omega(CH_2)$ $\nu_a(CH_2)$	763, –1358 (D), 1529 (G), 1632, –2904 (2D), 3406	$\gamma_\omega(CH_2)$	689 –690 1329

Earlier we investigated two-polar oscillations in absorption spectra of periodical 2D macroporous silicon structures with nanocoatings of SiO_2 and CdS nanoparticles. The optical absorption spectra we measured at normal incidence of IR radiation along the cylindrical macropores in the air at room temperature. Fig. 5 a, c show fragments of two-polar IR absorption in macroporous silicon structures and Fig. 5 b, d show fragments of two-polar IR absorption “polymer (PVC)–CNTs” composite. Giant two-polar oscillations of the absorption appear in the spectral region of Si-Si bonds and in the 5500–7500 cm^{-1} spectral region of P_b centers.

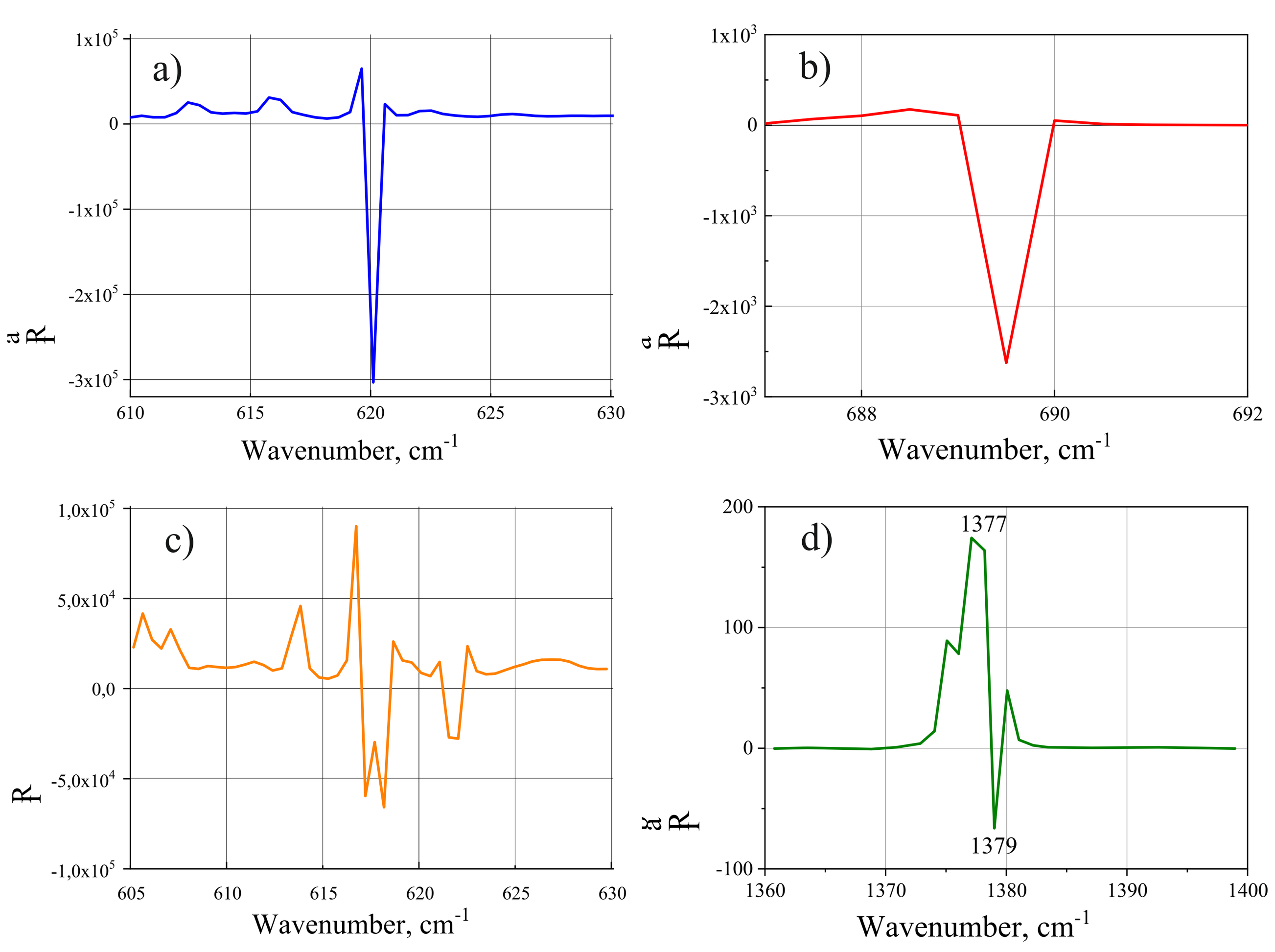

Fig. 5. Two-polar IR absorption in macroporous silicon structures (a, c) and “polymer (PVC)–CNTs” composites (b, d).

The application of high-resolution IR absorption spectroscopy is determined by detection of bipole-active TO vibrations, photon splitting and giant two-polar absorption oscillations with amplitudes of $\pm10^7$ arb.un. As a result, the dispersion law in *yz* surfaces of macropores change to *z* direction along macropores. The vertically polarized light along macropores (*z* direction) and horizontally polarized light (*x* direction) permit the explanation of results as two-photon interference (the Hong-Ou-Mandel effect). In this case, macropore is a beam splitter (BS) with maximum and minimum coincidences for measurements with parallel and perpendicularly polarizations, respectively. Beam splitter includes input ports A and B, and output ports labelled C and D. The four ways of the two photons can exit from the beam splitter through the same port or different ports. We observed constructive interference of the twophoton states corresponding to photons exiting through the same output ports (bosonic behavior). Two-polar resonances in $\pm z$ direction are connected with 1D polaritons (destructive interference of the two-photon states, fermionic behavior).

Earlier we used high-resolution IR absorption spectra to investigate periodical 2D macroporous silicon structures with nano-coatings of SiO_2 and CdS, ZnO nanoparticles. The application of highresolution IR absorption spectroscopy permitted to detect dipole-active TO vibrations, photon splitting and giant two-polar absorption oscillations with amplitudes of $\pm10^7$ arb. un. As a result, the dispersion law in *yz* surfaces of macropores change to *z* direction along macropores. It means additional degree of freedom as vertically polarized light in *z* direction and horizontally polarized light in *x* direction, beams splitting and two-photon interference – Hong-Ou-Mandel effect. In this case, 2D resonances of Wannier-Stark electro-optical effect in *yz* plane correspond to constructive interference of the two-photon states (bosonic behavior), and dipolar resonance in $\pm z$ direction is determined by destructive interference of the two-photon states (fermionic behavior). Bipolar oscillations of 1D-polaritons have the ultra-small half-width 0.4–0.6 cm^{-1} and minimal Rabi frequency of samples 1.0 cm^{-1} equaled to the resolution of spectral measurements.

Optical properties of crystals are determined by interaction of an external electromagnetic field with dipole-active states of the crystal bulk and with defects of crystal structure. This interaction leads to the formation of a linked state of the oscillate movement of charged particles (dipole) with the electromagnetic field, named polaritons. For 2D macroporous silicon structures with nanocoatings band bending on the surface of the macropores are significant. Under these conditions, surface polaritons interact with photons strongly due to resonances of dipole-active Si-Si-bond vibrations and surface modes on boundaries Si-SiO_2 and SiO_2+PEI-ncCdS on macropores. Si-Si-bonds represent the transverse fluctuations of silicon atoms on the surface of the macropores, i.e., transverse phonons.

Measurements the giant two-polar oscillations with very small half-width 0.5 cm^{-1} (Fig. 4) testify the strong interaction of surface polaritons with photons. Moreover, by changing the thickness of the nanocoatings, it is possible to achieve a match in the frequency of interference modes with frequencies of surface bond oscillations on boundaries Si-SiO_2 and SiO_2+PEI-ncCdS (slotted modes). When the frequencies of local oscillations of surface bonds and slotted modes matched, then the light absorption increases up to 10^5 times on the frequencies of slit oscillations of surface bonds. For macroporous silicon, 2D resonances of Wannier-Stark electro-optical effect in *yz* plane correspond to constructive interference of the two-photon states (bosonic behavior, 2D polaritons), and two-polar resonances in $\pm z$ direction are determined by 1D polaritons (destructive interference of the two-photon states, fermionic behavior). For composites polymer-CNT two-polar resonance in $\pm z$ direction are determined by 1D polaritons (destructive interference of the two-photon states, fermionic behavior) in spectral area of sp^3 hybridization bonds. When frequencies of local oscillations of surface bonds of carbon nanotubes and slotted modes along nanotube-polymer boundaries matched, then the light absorption increases in 10^2– 10^3 times (Fig. 4) on the frequencies of slit oscillations of surface bonds. Thus, vertically polarized light along carbon nanotubes and horizontally polarized light for D and 2D bands resulted in beams splitting and two-photon interference and quantum Hong-Ou-Mandel effect.

Conclusions

The opportunity to enhance the properties of nanostructured surfaces is demonstrated on “polymer–multiwall CNTs” composites. Influence of sp^3 hybridization bonds on polymer strengthening is investigated in composites polypropylene (PP), polyamide-6 (PA6), polyamide-12 (PA12) and polyvinyl chloride (PVC) after adding CNTs to polymers (concentration of 0.25 %).

IR absorption of “polymer–CNTs” films exceeds that of polymer by 10–10^3 times in the entire spectral range measured after adding nanotubes with concentration of 0.25 %. Higher C–C fluctuations, CH, CH_2 and CH_3 bond absorption correspond to higher absorption at the frequencies of γ_ω (CH) and γ_ω (CH_2) vibrations. In addition, two-polar IR absorption measured after adding carbon nanotubes to polymers with negative IR absorption at spectral positions of sp^3 hybridization bonds of “D-band” and of double “2D-band”. The light absorption increases 10^2–10^5 times when the frequencies of local oscillations of surface bonds in carbon nanotubes matched slotted modes along nanotube-polymer boundaries resulted in the photon beams splitting and two-photon interference – Hong-Ou-Mandel effect.