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Optical absorption spectroscopy and properties of single walled carbon nanotubes at high temperature

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ABSTRACT

Here, we present an experimental investigation of the optical spectra of single walled carbon nanotubes (SWCNT) at temperatures up to 1273 K. This investigation gives insights into the electronic structure of metallic and semiconducting SWCNT at different temperatures by measuring the shift of the S_{11}-, S_{22}- and M_{11}-band with optical absorption spectroscopy. We observed a decrease of the transition energies in both metallic and semiconducting SWCNT with increasing temperature determined by the shift of the S_{11}-, S_{22}- and M_{11}-absorption bands. The shifts follow the Varshni-equation. Furthermore, calculation of the average exciton binding energy (80–90 meV) in metallic SWCNT from the shift of the M_{11}-band was performed. We demonstrate in this paper, that the optical absorption spectroscopy is an effective tool for characterisation of the electrical properties and structure of SWCNT.

1. Introduction

SWCNT show many interesting electrical and mechanical properties and are promising candidates for e.g. high strength composite materials [1–3]. Each SWCNT has characteristic n,m numbers which describe the chirality and the electronic character of the tube. SWCNT can be seen as a single rolled up graphene sheet. The numbers n, m of a SWCNT define a vector $\mathbf{C} = n\,\mathbf{a_1} + m\,\mathbf{a_2}$ which shows the direction in which a graphene sheet needs to be rolled up in order to create the SWCNT with the chirality (n,m) (Fig. 1).

The semiconducting (sc) SWCNT can be divided in type I and type II with $(2n+m)\mathrm{mod}3 = 1$ and $(2n+m)\mathrm{mod}3 = 2$, resp. The metallic (m) SWCNT have $(2n+m)\mathrm{mod}3 = 0$. From a known (n,m)-chirality the SWCNT diameter d can be calculated using:

$$d = \frac{a\sqrt{n^2 + nm + m^2}}{\pi} \tag{1}$$

with $a = 0.246$ nm.

There are different techniques to investigate the diameter of SWCNT and chirality as electron microscopy or fluorescence spectroscopy [4,5]. Other common characterisation methods for SWCNT are optical absorption spectroscopy (OAS) and the resonant Raman spectroscopy. Using OAS, diameter distribution, purity or the relation between m- and sc-SWCNT can be assessed [6–8]. Both methods, the OAS as well as the resonant Raman spectroscopy, are attributed to inter-band transitions in SWCNT and are well studied in the last years [6,7].

The transition energy is e.g. dependent on the tube diameter d. By tight binding calculation a simple relation between nanotube diameter d and the transition energies $E_{sc,m}$ of sc- and m-SWCNT was defined [1,6,7]:

$$E_{sc,m} = 2i\frac{\gamma_0 a_{C-C}}{d} \tag{2}$$

with $i = 1$ for S_{11}, $i = 2$ for S_{22} and $i = 3$ for M_{11}; $\gamma_0 = 2.9$ eV is the nearest neighbour carbon–carbon interaction energy and $a_{C-C} = 0.144$ nm is the nearest neighbour carbon–carbon distance. $E_{sc,m}$ is the energy distance between the van Hove singularities and d is the tube diameter. However, because of discrepancies with experimental results different modifications and improvements of Eq. (2) were necessary to get a more accurate calculation of $E_{sc,m}$ and a better congruence with experimental results [9–12]. Saito et al. calculated the transition energy $E_{sc,m}$ by taking into account the exciton binding energy E_b between the electron and the hole, the self-energy Σ and the gap energy E_g between the valence and conduction band. The different energy contributions for $E_{sc,m}$ are shown in Fig. 2b. However, also the material which surrounds the SWCNT has an influence on the transition energy $E_{sc,m}$ [13]. A model for ambient effects on the transition energy $E_{sc,m}$ was introduced by Nugraha et al. [14]. They used for the calculation of $E_{sc,m}$ a

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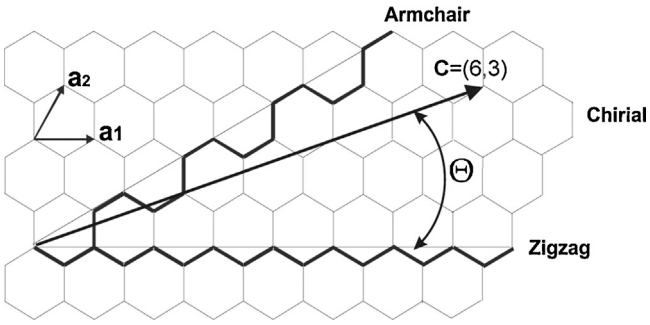

Fig. 1. The vector $C=(n\ a_1+m\ a_2)=(6\ a_1+3\ a_2)$ defines a chiral SWCNT (6,3). The SWCNT with $\theta=0$ or 30° are called zigzag or armchair tubes.

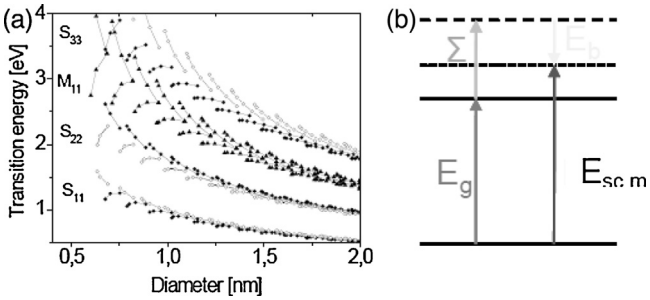

Fig. 2. (a) Kataura plot, calculated with the extended tight binding approximation and with $\kappa=2.22$ for bundled SWCNT (data provided by Saito et al. [14,16]) The transition energies for sc-SWCNT with full circles are $(2n+m)\mathrm{mod}3=1$ and with empty circles are $(2n+m)\mathrm{mod}3=2$. (b) The different energy contributions which are responsible for the transition energy $E_{sc,m}$. E_g is the gap energy, E_b is the exciton binding energy and Σ is the self-energy.

dielectric constant of $\kappa=2.22$. Saito et al. calculated and provided finally the transition energies $E_{sc,m}$ for any (n,m) chirality with respect to all known parameters [14–16]. The corresponding Kataura plot is shown in Fig. 2.

We demonstrate in this paper that the values shown in Fig. 2a are on good agreement to our experimental data and that the extensive calculation of the transition energy by Saito et al. delivers very exact values. Though there are different commercial SWCNT sources available, the structure of the SWCNT products is generally not well analysed. We measured the optical absorption of the SWCNT in inert atmosphere directly after the synthesis in order to avoid side effects of adsobates [8,13] and demonstrate the analysis by OAS based on the calculation from Saito et al. Furthermore we present for the first time OAS spectra of SWCNT at high temperatures. The information from these spectra expands the information content which can be gained by OAS. We show that the detailed theoretical analysis is well suited for room temperature characterisation of SWCNT, however at higher temperature the temperature dependence of the transition energy needs to be considered. Additionally we calculated e.g. the exciton binding energy in m-SWCNT by OAS at high temperature.

2. Experimental

SWCNT have been catalytically synthesised at 1273 K under constant conditions with a modified pulsed arc technique within a 7 m long custom-built tube furnace in nitrogen gas [17]. The setup is shown in Fig. 3. The synthesis takes place in zone 1 at 1273 K. Here, the anode is evaporated by a pulsed arc discharge. The graphite anode was doped with transition metals. During the cooling process of the evaporation plume the SWCNT grow. A more detailed description of the SWCNT synthesis process is presented in Ref. [18]. The synthesis products (35% SWCNT, 20% catalyst particles and 45% amorphous carbon) were swept downstream with an continuous gas flow of 5 cm s^{-1} and were finally collected in a gas scrubber at the end of the reactor. We synthesised a few hundred gram material per day.

Downstream, behind the 0.5 m long synthesis zone (zone 1), a 6.5 m long cooling zone (zone 2) was connected by a heat barrier to suppress any gas convection between the two zones. In the cooling zone, the tube furnace temperature was adjusted to temperatures between 373 K and 1273 K, depending on the experimental needs. At the end of the cooling zone, two side-tube connectors with windows opposite to each other were used for the in-line OAS characterisation of the aerosol stream inside the tube furnace [19]. The main advantage of this approach is that the SWCNTs were kept freely floating within the aerosol stream in the inert gas stream, thus avoiding any unwanted contributions from substrate clamping as well as contributions from adsorption and functionalisation effects from gaseous impurities like oxygen or water. Two spectrometer, the NanoSpectralyzer NS1 and the Brucker Matrix F were used to measure the metallic and semiconducting absorption bands. From the obtained 50 spectra of nanotube material at the selected temperatures, the positions of the most relevant optical SWCNT features, the S_{11} and S_{22} absorption bands for sc-SWCNTs and the M_{11} absorption band for m-SWCNTs, have been determined. The calculated mean transition energy $E_{sc,m}$ remained very close around a mean value (within a few meV) for each temperature. This provided sufficient measurement accuracy for our experiments.

3. Results and discussion

Selected in situ measured single spectra at 673 K are exemplarily shown in Fig. 4.

A detailed analysis of the averaged absorption bands at room temperature is shown in Fig. 5. The S_{11}-, S_{22}- and M_{11}-absorption bands are a superposition of contributions from many SWCNT which contribute to the absorption bands. The arrows in Fig. 5a, b and c show the energy positions where a particularly large

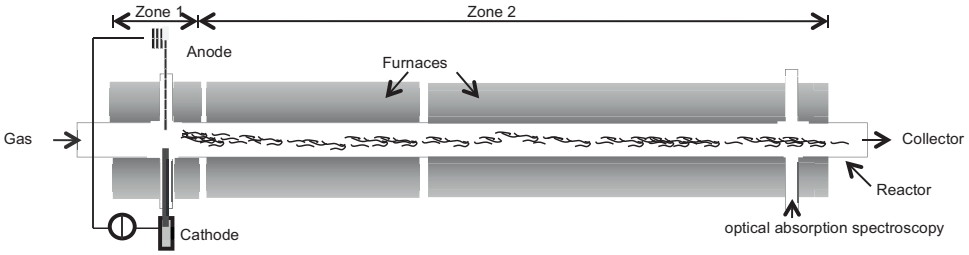

Fig. 3. In zone 1 the SWCNT synthesis takes place at 1273 K. In zone 2 the temperature was changed between 373 and 1273 K. At the end of the furnaces the optical absorption spectroscopy was done.