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Significant decrease in the reflectance of thin CNT forest films tuned by the Taguchi method

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A B S T R A C T

The Taguchi method of design of experiments was utilized to tune the optical properties of a carbon nanotube (CNT) forest by decreasing the total ultraviolet-visible (UV-Vis) reflectance. The CNT growth parameters included the acetylene flow rate, the thickness of the Fe catalyst film, substrate polarization potential (bias) during sputtering of the AlO_x buffer layer, and acetylene-to-hydrogen gas flow ratio. A plot of the signal-to-noise (SN) ratio showed that the buffer-layer bias and catalyst thickness had the highest impact on the final results of the total optical reflectance. A verification experiment was conducted based on the optimized values of the growth parameters, and it yielded a 45% decrease in the UV-Vis reflectance to the lowest value (0.077% at $\lambda = 750$ nm) ever reported for a thin CNT forest film with relatively low height (~20 μm). In addition, the structural parameters of the CNT forest were studied. The effects of the CNT structure (single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multi-walled CNTs (MWCNTs)), filling factor (density), and alignment of CNTs on the total optical reflectance were investigated. The density and alignment of CNTs showed the highest impact, while the individual CNT structure exhibited a negligibly small effect on the low total optical reflectance.

1. Introduction

Since the first work published by Iijima in 1991 [1], the unique structure and exceptional electrical, physical and optical properties [2,3] of carbon nanotubes (CNTs) have gained much attention in various fields of science. Vertically aligned high-density CNT forests can provide CNTs with suitable length, diameter, and properties for mass scale production [4]. Physical properties of individual CNTs have a direct effect on mechanical, electrical, thermal, and optical properties of CNT forests, thus, various CNT forest structures were used for different applications, such as nanoelectronic devices [5,6], field-effect-transistors (FETs) [7–9], a wiring material for large-scale integrator (LSI) interconnects [10,11], actuators and polymeric composites for electronic devices [12], and high current density emitters [13–15]. Optoelectrical properties of CNTs were also used for the fabrication of various types of solar cells, in which CNTs act as electrodes [16,17], counter electrodes [18,19], active layers [20] and conducting scaffolds for semiconductor materials [21].

CNT arrays possess unique nonlinear optical properties [22–24], which have their origin in a high third-order susceptibility with very fast regeneration time [25,26]. Under the external electromagnetic radiation, the behavior of single-walled carbon nanotubes (SWNTs) is similar to direct gap semiconductors and their absorption spectra are usually dominated by exciton lines [24,27]. Low density, vertically aligned CNT forests possess low refractive index and due to their unique structure, which can trap light very effectively, CNTs exhibit superior light absorbance properties [28–30]. A very high absorption and low reflectance in the visible (Vis) and infrared (IR) regions [29–31], resembles the properties close to that of a black body, a theoretical material, which is claimed to absorb all spectra of incident light. Various groups presented results of very low reflectivity of CNT forests, with the lowest reflectance of incident light in the ultraviolet-visible (UV-Vis) range of 0.045% noted by Yang et al. [29] for 633 nm wavelength, for the CNT forest height of 200–300 μm. On the contrary, recently presented Vantablack CNT coatings, which are claimed to be the darkest material ever created, showed a very low infrared reflectance, below 0.1%, across the 2.5 μm–15 μm wavelength range, for CNT forests of 20–50 μm height, while in the Vis range the reflectance was below 0.2%

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[32]. Moreover, some applications, like energy storage devices, CNT metamaterials for heat absorption, superlenses, and terahertz antennas require high absorbance and small size of the elements, which with the decrease of the height of CNT forest would result in the decrease of the total absorbance. An example of such are metamaterials [27,33,34], which properties are derived from a shape and size of designed structures, and also from properties of the material that consists of those structures. For that reason, the density, alignment and other parameters of CNT forest should be tuned in order to obtain the desired response of metamaterials at various frequencies. One of the most important features of CNTs, which should be addressed in metamaterial applications, is the total reflectance of CNT forest, which values should be as low as possible [33].

Although in several experiments, a very low total reflectance was achieved, mechanisms responsible for the variation of the absorbance are still not clearly explained. The investigation of the influence of the height of vertically aligned multi-walled CNT (MWNT) forest [35] showed the variation of the absorbance, in relation to the forest height, while the study of individual CNTs and the effect of the chirality on the total reflectance, also revealed a strong dependence between CNT structure and results [36]. Moreover, simulations of the electromagnetic response of CNT arrays, using a finite-difference-time-domain (FDTD) method, were also conducted, in order to study effects of structural randomness, such as random position, diameter, length, and orientation [36], and also to investigate the total visible absorbance of two-dimensional nanotube arrays [37].

To meet the demands posed by future applications of CNTs, various growth methods, such as arc-discharge, laser ablation or chemical vapor deposition (CVD) are utilized, among which the CVD method is the most commonly used [38]. A thermal catalytic CVD (CCVD) is a cheap and simple method, which provides a high yield and a relatively high purity of CNTs, and allows for an easier control of growth parameters and structures [38]. Despite the fact that in recent years a great improvement has been made to the growth control of CNTs, a further improvement of density, alignment, and optical properties, especially already high absorbance of CNT forest became very challenging, due to a large number of process parameters influencing the CNT growth [39–42], starting from catalyst preparation methods and finishing on annealing and growth processes. Also, the enhancement of absorbance of relatively short CNT forests is even more difficult. Testing possible parameters separately and choosing the most suitable values can be a time-consuming process, requiring a large number of experiments and still, it may be difficult to find the most suitable values of parameters, which meet the demands. One of the possible solutions is to decrease the number of experiments by applying optimization methods to the design of the experiment parameter matrix [43]. These methods include, but are not limited to, a randomized complete block design (RCBD), a full and fractional factorial designs, a central composite design, and a Taguchi method. The RCBD method is used to optimize only one, factor (primary factor), which is supposed to be the most relevant for the process variation, while both types of factorial designs allow for the optimization of multiple factors; however, only at two different levels per factor. The central composite design is an extended full factorial design, which adds additional points (a central point and the star points) for more advanced analysis and similar to factorial designs, allows for the multifactorial optimization with two levels of parameters. Finally, the Taguchi method, which is also based on the fractional factorial design, but also orthogonal designs, was developed to optimize values of controllable parameters and allows for tuning of multiple factors with many levels per each parameter. The Taguchi method introduces a parameter design to make the process less variable in the face of uncontrolled variation, and a tolerance design to specify how and when the quality of the product can be enhanced. This method allows for the multifactorial target-oriented optimization, in which the quality loss function is tuned to improve the average properties of the product while keeping the standard deviation low. For the optimization of reflectance of CNT forest, the investigation of independent growth parameters is required and only the Taguchi method allows for optimization of the complex system of dependent parameters. Moreover, the reproducibility and stability of the process are crucial, thus, in order to increase reliability and to investigate critical factors among the investigated parameters, which were responsible for the for the decrease of the UV-Vis reflectance, the Taguchi method was applied for the optimization of four growth parameters with three different values.

The Taguchi method allows for the screening of factors and the identification which are relevant for explaining process variation. This method can be applied for systematic investigation of the process and parameters that influence the quality of the final product [44–46] to improve manufacturability, reliability, and quality of a product. The Taguchi method is based on a systematic approach, which allows for the control of multiple factors, in order to reduce or eliminate the variation of results and adjust the process on target at the same time. In robust design, changes of properties of the product dependent on noise factors (N – Noise) are minimized (fluctuations of uncontrollable parameters), while changes correlated to signal factors (S – signal) are maximized (yield, density, alignment, etc.). The Taguchi method provides a statistical coefficient η (Signal-to-Noise ratio, SN ratio) for the response analysis of selected physical quantities. The η coefficient is the only measure of robustness in the Taguchi method and allows evaluation of the influence of each parameter on properties of the product. In this method, information about statistically significant factors are provided by the SN ratio analysis and experimental data analysis, and optimum levels of parameters are selected [44,47–49]. By the analysis of SN ratios, the reproducibility and stability of the process are increased, while occurring fluctuations are minimized. In the Taguchi method, 3 main optimization targets are utilized: the smaller-the-better; the larger-the-better and nominal-is-best. In this work, in order to tune optical properties of CNT forest, by decreasing the total reflectance in the Vis regime, the criterion 'the smaller-the-better' was applied, by adapting the equation for the SN ratio coefficient η:

$$\eta = -10\log_{10}\left(\frac{1}{\mathrm{n}}\sum_{\mathrm{i}=1}^{\mathrm{n}} y_{\mathrm{i}}^{2}\right)$$

where y_i is the response to signals and n is the number of repetitions of each experiment.

For the purpose of experiment planning, the Taguchi method introduces orthogonal arrays, a system of experimental tables which allow for a calculation of the maximum number of an independent (orthogonal) main characteristics of the product with a minimum number of experiments [44]. In recent years, the Taguchi method proved to be useful also in the CNT field, in which the optimization of the CNT growth [50–53], catalyst formation conditions [47], field emission properties [54], and various applications of CNTs [55,56]; however, none of these works regarded tuning optical properties through optimization of growth parameters.

The purpose of this study is to investigate the effects of the CNT growth parameters using the Taguchi experimental design, in order to tune optical properties, through a decrease of the total reflectance of the UV-Vis light in short CNT forest (~20 μm). The work is focused on the examination of the optimum combination of growth parameters resulting in the decrease of the reflectance, and the investigation of the variation of CNT forest structure (crystallinity, density, alignment, etc.) responsible for the results. The procedure of synthesis of CNT forest by the thermal CCVD includes many steps, which may cause low reproducibility and reliability of the process [57,58]. By employment of the Taguchi method, however, it is possible to decrease or eliminate negative effects of the production process by minimization of the negative influence of noise factors. For various industrial applications, high UV-Vis absorption materials are necessary; however, for most of the cases, the height of the highest absorbance CNT forest is above 200 μm. In this work, it was reported that remarkably low total