論文内容の要旨

The extraordinary electrical, chemical, physical and optical properties of carbon nanotubes (CNTs), like an anisotropic electrical conductivity of horizontally aligned CNTs, and anisotropic optical absorption of vertically aligned CNTs are directly derived from their unique structures. Highly controlled synthesis process including self-organization of the catalyst particles is desired to achieve unique highly oriented periodically positioned CNT forest for new electronic and optronic applications.

CNT act as a nearly ideal one-dimensional nano-rod antenna with a diameter of a few nanometers and length to many micrometers. The behavior of single-walled CNTs (SWNTs) is similar to direct gap semiconductors with absorption spectra dominated by exciton lines. The nonlinear optical behavior of CNTs is related to high third-order susceptibility with sub-picosecond recovery time, in which the source of the nonlinearities is an effect of the saturation of the resonant excitation lines and allows many various applications like light sources in nanoscale, photodetectors or metamaterials.

Metamaterials are artificial materials engineered to obtain properties that do not exist in nature and acquire their properties from embedded subwavelength structures grouped together to exhibit the required values of permittivity and permeability in the desired frequency range in order to manipulate electromagnetic waves. Properties of metamaterials are derived from a shape and size of designed structures and from the properties of the material that consist of those structures. Currently, metamaterial development is limited by the design and fabrication methods; however by utilizing anisotropic materials, like CNTs, it those limitations can be overcome. High shielding effectiveness accompanied by a high dielectric constant of SWNTs can be tuned by a control of growth parameters and post-processing operations such as chemical treatment or molecular functionalization, what is not possible with conventional materials like metals. Due to that, unique structure and properties of CNTs influence the performance of metamaterials and can be used for the designing of metamaterials. Finally, for the manufacturing of electromagnetic metamaterials, the development of (1) structure control of CNTs diameter (in 1 – 100 nm) and (2) height (10 nm – 10 μm), the design of an electromagnetic circuit for CNT forest metamaterials, and (4) patterning process has to be investigated.

In order to successfully fabricate CNT metamaterials, highly controlled CNT forest synthesis process is required. Unfortunately, the growth of CNT suffers many difficulties in finding optimum growth parameters, reproducibility, and mass-production, related to the large number of parameters influencing synthesis process. Choosing the proper parameters can be a time-consuming process, and still may not give the optimal growth values. One of the possible solutions to decrease the number of the experiments is to apply optimization methods to the design of the experiment parameter matrix. By applying statistical methods, like Taguchi method, the stability, reproducibility can be improved.

The aim of the first part of the research was to synthesize uniform, high-aligned and small diameter SWNT forest which could support the fabrication of metamaterials. For that purpose, the Taguchi method of designing experiments was applied to optimize the formation of the iron catalyst particles during annealing process by analyzing average roughness and size of particles. The annealing parameters optimized during the series of experiment were: annealing time, hydrogen flow rate, temperature and argon flow rate. Based on the obtained results, plots of signal-to-noise (SN) ratios were prepared and showed that the temperature and time of annealing have the highest impact on average roughness and size of the Fe particles. For more detailed study of the influence of parameters, the interaction plots of tested parameters were prepared. The results of experiments and Taguchi statistical analysis of SN ratios, sensitivity and mutual interactions demonstrated that Ostwald ripening and subsurface diffusion of catalyst atoms into AlOx support were basic mechanisms responsible for the formation of catalyst particles. Further analysis of the results confirmed that temperature and time are main parameters inducing those mechanisms of the reduction of particle size, supported by additional H2/Ar annealing atmosphere. Finally, physical model of the catalyst formation process was provided for the first time with the support of statistical calculations, proving that the Taguchi method is very useful in planning the experiments and analysis of obtained results. Moreover, the Taguchi method allowed decreasing the number of experiments from 256 to 16, keeping the same reliability and accuracy at the same time.

For the final evaluation, CNT forests were grown on silicon substrates with AlOx/Fe catalyst by thermal chemical vapor deposition method. Based on obtained results, the average diameter of CNTs was decreased by 303% by decreasing diameter from 9.1 nm (multi-walled CNTs) to 3.0 nm (single-walled CNTs).

CNT forest is known as a material for blackbody absorbers. For the fabrication metamaterials, high-absorbance SWNT forest is required. For that reason, in the second part of the research, the Taguchi approach of the designing experiment was utilized to tune optical properties of CNT forest by decreasing the total optical reflectance, which is required for future application to metamaterials. The annealing parameters optimized previously remained unchanged, while the other parameters related to catalyst deposition and CNT growth were optimized. The optimized parameters were: acetylene gas flow rate, Fe catalyst film thickness, substrate polarization potential (bias) during AlOx buffer layer sputtering, acetylene/hydrogen gas flow ratio. SN ratio graph showed that bias during the deposition of buffer layer and the thickness of the catalyst have the highest impact on final results of total optical reflectance. It was concluded that bias during the deposition of AlOx layer changes the inner structure of the films and affects the process of Fe catalyst formation, resulting in various size and density of Fe particles. On the other hand, higher thickness of Fe catalyst supplies more material during annealing process and allows the formation of a higher number of particles on the surface, improving the density of CNT forest. Based on the optimized values of the growth parameters a verification experiment was conducted, and it yielded a 45% decrease in the reflectance to the lowest value (0.077%) ever reported for a CNT forest with relatively low height (~21 μm). Furthermore, the study of structural parameters of CNT forest was conducted. In addition, the structural parameters of the CNT forest were studied. The effect of the structure of the CNTs was studied by obtaining Raman spectra of the grown CNT forest. It was found that for a homogeneous, vertically aligned CNT forest, the effect of the type of CNT (SWCNTs, DWCNTs, or MWCNTs) was insignificantly small and could be neglected. There was no observable relationship between the CNT type and values of total reflectance. Furthermore, the analysis of influence of the filling factor (density) and alignment of CNTs on the total optical reflectance was investigated for the first time. It was concluded that the density and alignment of CNT forest have significant impact on the total reflectance.

Low-temperature growth of CNTs on Al foil at 600°C requires treatment of the surface, in order to remove contaminations present on the samples. It was confirmed, that both, utilizing of AlO_x buffer layer and hydrogen treatment of surface, before deposition of Fe catalyst, have positive effect on the growth of CNTs. The dependence of hydrogen annealing time showed, that 15 min of hydrogen annealing allows growth of relatively high density CNTs on the surface. Water-assisted CVD improved the low-temperature growth of CNTs on Al foil at 600°C, from 14.7 μm (w/o H2O) to 24.4 μm (0.07 sccm H2O) for 10 min growth. Furthermore, the investigation of catalyst thickness showed that Fe catalyst thickness of 1.0 and 1.2 nm are the most suitable for low temperature growth. Catalyst thickness of 0.8 nm, due to high roughness of Al foil surface, did not allow growth of high-density CNTs. Due to slower growth of thicker MWNTs, low height of CNT forest, for thicker catalyst was observed. Due to water-assisted CVD, the catalyst activity was improved to 120 min, allowing growth of 119±15 μm CNT forest.

After obtaining high-absorbance SWNT forest, the fine patterning of CNT forest were investigated. Due to size limitations and high precision requirement, the focused ion beam (FIB) method was chosen. Fabrication of CNT forest nanostructures in the range of hundreds nanometer to several micrometers is a relatively new problem and due to that reason, a focused ion beam (FIB) method was chosen. The FIB proved a possibility of fabrication of metamaterial patterns in metals. The FIB method is maskless and allows fabrication of nanoscale patterns of various shape and size; however, due to sputtering, redeposited material is observed on the surface out-of-patterned area. To overcome this disadvantage, a secondary etching method was proposed to clean the patterned surface from the redeposited material. The FIB secondary etching method allowed uniform and fine patterning of CNT forest nanostructures for metamaterials. Furthermore, due to the fact that the electromagnetic behavior of CNT metamaterials is still unknown, small area fabrication of various patterns was conducted.

This part of the work presents the combination of precise FIB patterning process with additional secondary FIB etching steps to remove redeposited material from the surface and improve the growth of CNT forest in the SRR array nanostructures. This method allows fabrication of nanoscale metamaterial patterns and catalytic growth of high-density CNT structures as small as about 190 nm on pre-deposited catalyst film in designated areas. The patterning depth of 10 nm and the secondary etching of 0.5 nm allowed the growth of high-aligned CNT forest nanostructures. Additionally, the influence of FIB etching depth on the morphology of catalyst surface and growth of CNTs has been investigated.

The effect of the secondary etching was determined by the amount of removed material. During the patterning of SRR arrays, the sputtered material was mainly redeposited on the edges of patterns, forming ridges, and in the smaller degree in the middle of the walls. Furthermore, it was assumed that the mass density of the redeposited film is lower than the mass density of catalyst film, and due to that, the sputtering rate is high, resulting in faster etching at the ridge area. By applying secondary etching of 0.5 nm, the majority of resputtered material and top layer of Fe catalyst film were removed. By cleaning the surface and decreasing the thickness of Fe catalyst, the improvement in the growth height and uniformity was observed. Moreover, thinner catalyst allowed growth of high-crystallinity and low defect SWNTs with higher growth rate.

The successful development of fabrication method of CNT metamaterial nanostructures allowed the investigation of exceptional properties of carbon nanotube metamaterial. In the final part of the work, IR properties of various CNT forest patterns for metamaterials, prepared on the predeposited catalyst, was presented for the first time. The bulk properties of patterned self-standing uniform CNT forest in the IR region were investigated. The infrared reflectance of CNT metamaterial patterns was presented, showing high dependence on shape, height, alignment and pitch of the patterns. Furthermore, the trail of tuning of magnetic resonance of CNT patterns was presented. The influence of CNT metamaterial patterns on the IR absorbance was studied. The dependency of patterned SWNT forest height, shape, pitch, alignment and magnetic resonance control was investigated showing considerable influence on the total IR reflectance spectra. The increase of height of patterned CNT forest reduced the reflectance. It was confirmed that the absorption of infrared radiation was increased by the formation of dip shape as resonator role in SRR patterns, not to the total absorption area ratio covered by CNTs. The tuning of resonance of CNT patterns showed insignificant changes in the FT-IR reflectance spectra. Furthermore, the decrease in the value of the spacing S between the patterns caused the reduction of reflectance and the shift of the phase of oscillations was observed. Apart from that, the control of the alignment from the horizontal to vertical resulted in the change of the absorbance and significantly changed the phase of oscillations, due to the changes in the propagation of an electromagnetic wave through the designed CNT structures composed of horizontally aligned CNTs. Finally, compared to the typical gold (Au) patterns, we were able to control the alignments, density, and height of CNT patterns which significantly influenced the IR reflectance spectra. During the experiments, the resonance, typical for metamaterial structures was not observed. It was assumed that the potential reason was related to high absorption in CNTs, and also due to the transverse direction of IR radiation to the CNT axis.

In conclusion, the optimization process allowed a growth of a high-density and high-aligned SWNT forest with very low reflectance, which was required for the successful fabrication of metamaterials. By applying a FIB patterning process followed by newly developed FIB secondary etching method, the uniform and fine fabrication of CNT metamaterial nanostructures was possible, in various sizes, shapes and diversity. Finally, the investigation of IR properties of patterned SWNT forest for metamaterials showed the influence of shape, height, alignment, spacing, magnetic resonance tuning on the electromagnetic response in the IR regime, proving a successful fabrication of CNT metamaterials.