NANOMATERIAL SYNTHESIS AND NANODEVICE FABRICATION BY LASER CHEMICAL PROCESSING

by

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The main objective of this dissertation is to explore the possibility and extend the capability of laser-technology into nanoscale material processing. The research focused on three novel laser chemical processing techniques for nanomaterials processing, including 1) near-field-induced spatially-confined photochemical deposition of diamond-like carbon (DLC) films on nanostructures; 2) pulsed-laser disintegration of inorganic compounds as nanocatalysts for large-area carbon nanotube (CNT) growth; and 3) laser-assisted chemical vapor deposition (LCVD) growth of CNTs and direct fabrication of CNT field-effect transistors.

In the study of near-field induced photochemical deposition of DLC films on nanostructures, DLC was deposited on tungsten nanotips as well as Mo nanowedges using benzene as the precursor. Theoretical as well as experimental results confirmed the prediction of spatially confined and phase graded deposition of DLC film on sharp edges due to local intensity gradient of optical near field. We also developed a method to produce nanocatalysts by irradiating dispersed $NiSO_4$ microclusters on silicon substrates using a KrF excimer laser. Under appropriate laser fluences and multiple laser pulses, the disintegrated $NiSO_4$ nanocatalysts were used for large-area uniform multi-walled carbon nanotube (MWNT) growth. In the study of LCVD synthesis of CNTs, we have developed controlled synthesis of vertically-aligned CNFs, large-area high-quality MWNTs, and defect-free single-walled nanotubes (SWNTs) with different catalysts, carbon feedstock, and laser parameters. The synthesis could be achieved by both far-infrared CO_2 laser (10.6 μm) and near-infrared Nd:YAG laser (1064 nm) in a localized manner. The LCVD technique was also applied for direct fabrication of field-effect devices. Due to the unique advantages of the LCVD process, such as fast and local heating, as well as its potential to select chiralities during the growth, it may provide new features and versatilities in device fabrications.

DEDICATION

This dissertation is dedicated to Mom, Dad and my wife, Linna with love.

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CHAPTER 1

INTRODUCTION

1.1 Background and motivation

Since the advent of lasers in the 1960s, laser material processing has become an expanding field and been well established in a wide variety of industrial applications. Some of the mature areas include laser welding, soldering, drilling, and cutting in laser mechanical technology,[1,2] laser hardening, rapid solidification, glazing, cladding, and powder metallurgy in laser metals technology,[2,3] and laser recrystallization, doping, and annealing in semiconductor technology.[4,5] Owing to its unique features, laser technology provides flexibility and precision in material processing in automotive, aviation, medical instrument, and electronics industries. Tremendous research efforts have also been made in advancing laser material processing in microelectronic, data storage, and photonic applications. However, for a very long time, the inherent diffraction limit of laser wavelengths has constrained applications of conventional laser material processing in nanotechnology. To achieve nanoscale laser material processing, it is imperative to overcome the diffraction limit, which can only be realized by fundamental scientific innovations.

Currently, there are several important research directions, in which intensive laser nanoprocessing studies are being carried out: 1) to develop short wavelength optical source and optics, down to X-ray range[6-9]; 2) to develop ultrafast laser machining with current advances in femtosecond to future attosecond laser processing;[10-12] 3) to develop near-field related optical nanoprocessing, which is one of the most promising directions for next-generation nanolithography;[13-18] and 4) to develop laser techniques utilizing nanopatterns for nanoimprinting.[19-21] Most of these techniques address material removal or substrate patterning with high precision and controllability at nanoscales. Although it is of significant research and practical value, highly-controlled deposition of materials on nanostructures is rarely studied and many fundamental phenomena are yet to be explored. As a result, there are tremendous research needs in developing advanced techniques for high-quality nanoscale material synthesis and deposition with a high controllability in the material property as well deposition positions.

In this dissertation, our endeavourers are extended to explore the capability of

laser-based nanoprocessing techniques for controlled deposition and synthesis of nanoscale materials, such as diamond-like carbon films, and carbon nanotube/carbon nanofiber structures. In addition, fundamental understandings of the process mechanisms and their implications were also systematically studied. Within the framework of this objective, the research projects mainly focused on using laser for nanoscale material synthesis, including: 1) laser-assisted deposition of diamond-like carbon films on nanotips and nanowedges induced by near-field photochemical processing; 2) laser chemical vapor deposition (LCVD) of carbon nanotubes and carbon nanofibers, which was further applied to the fabrication of carbon nanotube field-effect transistors.

The research projects have the following significances in terms of academic contribution and industrial impact. For the study of near-field-induced position-controlled DLC coating on nanostructures, 1) it is a controllable surface process which extends surface coating to nanoscales in three dimensions, which bears major scientific interests in fundamental research; 2) it is a technique directly addressing the needs for coatings on sharp tips and edges of nanostructures, especially as self-lubricating and protective coatings for extensive wear applications at nanometric levels. For CNT growth using LCVD techniques, we not only established an independent CNT growth technique for high-speed, position-controlled CNT growth. In addition, this technique has successfully been applied to the fabrication of field-effect transistors, which bears great potential for electronic property control during growth by CNT-chirality selection.

1.2 Dissertation outline

This dissertation focuses on applying laser-based physical/chemical processes to nanoscale material processing and device fabrication. The entire dissertation is divided into seven chapters. In chapter 1, the motivation of this project and the dissertation outline are introduced. Chapter 2 elucidates the background and history of three important aspects of this project: 1) laser-assisted chemical processing, 2) diamond-like carbon material (properties, preparation, and applications), 3) carbon nanotube material (properties, synthesis, applications, and current limitations). Chapter 3 describes film deposition of diamond-like carbon on nanostructures controlled by laser-induced near fields. Both theoretical and experimental studies on enhanced optical near-field induced photochemical are described. Chapter 4 describes pulsed excimer laser nano-fragmentation of compound particles. This technique was applied to generating highly-uniform nanocatalysts for large-area synthesis of CNTs. Chapter 5 presents laser CVD synthesis of CNTs. In this chapter, a detailed study using CO_2 and Nd:YAG laser for nanofiber/nanotube material is introduced. The mechanisms of LCVD process for CNT growth are also discussed. In chapter 6, we extend LCVD technique in direct fabrication of CNT field effect transistors. The CNT growth can be conducted in a position- and direction-controlled manner. There is great potential in LCVD technique that it can achieve chirality selection during *in-situ* growth, which tackles the biggest challenge for lack of control of chirality-related electronic properties. Chapter 7 concludes this work with a summary of important results.

CHAPTER 2

BACKGROUND AND REVIEWS

2.1 Introduction to laser-assisted chemical processing

2.1.1 Laser-assisted photochemical processing

Laser photochemical processing is one of the most active areas in laser material processing, which can efficiently assist etching and thin film deposition via chemical methods. Through laser chemical vapor deposition (LCVD) method, a variety of materials, such as metals (from metal halides, alkyls and carbonyls), semiconductors (amorphous and crystalline Ge, Si, and compound semiconductors), insulators (oxides and nitrides), and heterostructures can be deposited.[22,23] Table 2.1 summarizes typical materials, their feed-sources and wavelengths for these applications.

Laser light can induce chemical reactions either homogenously within the gas or liquid phase, or heterogeneously at molecule-solid or solid-solid interfaces. In general, laser chemical processing involves both photothermal and photolytic processes. In photothermal process, multiple photons in the Vis-IR range must be absorbed to elevate the molecules to higher vibration levels until atoms are ionized or molecules are dissociated. In photolytic process, by absorption of UV-Vis photons, molecules can be directly dissociated by electronic dissociation in a single step.

A simple model[22] , as shown in Fig.2.1, will be used to briefly explain such complex processes. Let A and A^* characterize the system in the ground state and excited state, respectively. By assuming that there is no spontaneous emission, non-radiative transitions $A^* \rightarrow A$ are described by the thermal relaxation time, τ_T. The characteristic time for reaction of A and A^* with C are $\tau_A(T)$ and $\tau_{A^*}(T)$. At low excitation rates, where $\tau_T \leq h\upsilon / \delta I$, (δ is the excitation cross section), if $\tau_T << \tau_{A^*}$ and $\tau_A << \tau_{A^*}$, the excitation energy is immediately dissipated into heat and the reaction is thermally activated; if $\tau_T > \tau_{A^*}$ and $\tau_A << \tau_{A^*}$, the process is mainly photo-chemically and photolytically activated, during which the reaction takes place via excited species A*; if $\tau_T << \tau_{A^*}$, τ_A and $\tau_{A^*} << \tau_A$, or if all these time periods are comparable, both the 'thermal channel' and the 'photochemical channel' need to be considered.

TABLE 2.1 Laser chemical depositions of various materials.

Deposited material	Carrier gases	Substrate	Laser/wavelength (nm)	Ref.
Ag	$AgCF_3SO_3$, $AgPF_6$, $AgBF_4/C_6H_5CH_3$	Glass, SiO_2	HeCD 325	24
Au	$Au(CH_3)_2(acac)$	Si	Ar 515	25
Au	$HAuCl_4$/aq.	(100)Si	p-Nd:YAG 532	26
Fe	$Fe(CO_5)$	Al_2O_3, (100) GaAS	ArF 193, KrF 248	27
Fe	$Fe(CO_5)$	(100)Si	Hg lamp	28
Ni	$Ni(CO)_4$/He	Si	Ar 515	29
Ni	$Ni(CO)_4$/Ar	Glass	CO_2 10.6um	30
Si	SiH_4	SiO_2	KrF	27
Si	SiH_4	SiO_2	CO_2 10.6um	31
GaAs	$Ga(CH_3)_3$+AsH_3/ H_2	(100) GaAs	Ar 458-515 ; Nd:YAG 532	32,29
C (diamond)	2%CH_4+H_2	(100)Si ,	CO_2 10.6um	33
C (diamond)	0.5%-2%CH_4+H_2	Si	ArF 193	34,35
C (diamond-like carbon)	C_6H_{12}	Si	KrF 248	36,37

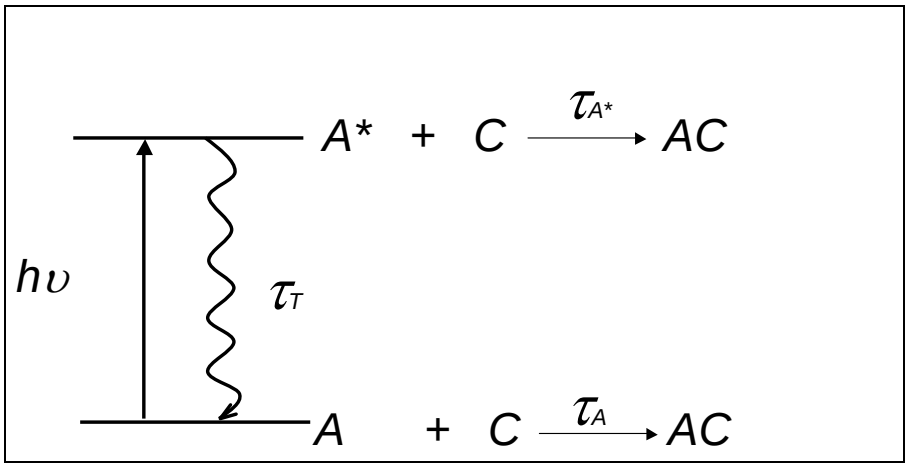

Fig. 2.1 Schematic diagram for photo-thermal and photochemical reactions.

For photo-thermally activated reactions, the net reaction rate can be described by

$$W(x,t) = k(T)N^{\gamma_{AB}}{}_{AB}N^{\gamma_{CD}}{}_{CD}\cdots = W_0(x,t)\exp(-\frac{\Delta E}{k_B T(x,t)}) \ , \qquad \text{(Eq. 2.1)}$$

where rate constant $k(T) = k_0 \exp(-\frac{\Delta E}{k_B T(x,t)})$ follows the Arrhenius law; ΔE is the apparent chemical activation energy; $N^{\gamma_{AB}}{}_{AB}$ is the density of the species, k_0 is a pre-exponential factor whose dimension depends on the total reaction order; and $T(x,t)$ is the temperature distribution and γ_i is partial reaction order.

For photolytically (photo-chemically) activated reactions the rate

$$W(x,t) = W_o' \prod_i [{}^{(n)}\sigma_i (\frac{I(x,t)}{h\upsilon})^n]^{\gamma_i} = k'(I)N^{\gamma_{AB}}{}_{AB}N^{\gamma_{CD}}{}_{CD}\cdots, \qquad \text{(Eq. 2.2)}$$

where $W_0' = k'_0 N^{\gamma_{AB}}{}_{AB}N^{\gamma_{CD}}{}_{CD}\cdots$, and $k'(I) = k_o' \prod_i [{}^{(n)}\sigma_i (\frac{I(x,t)}{h\upsilon})^n]^{\gamma_i}$, k_o' and thereby W_0' depends on the relaxation time relevant for selective excitation of species. Eq. (2.2) denotes the product over all species to be exited. As an example, single-photon excitation with a single type of reactant, *AB*, which can be characterized by *i=AB*, *n=1*, γ_{AB}=1,

$\gamma_{CD} = 0$. The rate constant is, $k'(I) = k_o'\sigma_{AB}\frac{I}{h\upsilon}$, where σ_{AB} is the single-photon excitation cross section. It is found that various gas-molecules have different excitation cross sections under different wavelengths.

2.1.2 Near-field induced photochemical process

Optical near-field theory, especially, light interaction with small particles, sharp tips, and tapered fibers, was developed in recent decades and in particular after the discovery of the surface enhanced Raman scattering (SERS)[38,39]. In 1980s, many theoretical works were carried out on the SERS phenomenon. It suggested that the enhancement was a result of a number of electrostatics effects,[40,41] surface plasmon effects[42] and electrodynamic effects,[43] and their combinations.[44] In brief, the local electromagnetic field that excited molecules adsorbed on a rough surface of some metals could be considerably greater than the field of the primary beam that interacted with the same molecules in the liquid or gas phases.

Based on theories of SERS, scanning near-field optical microscope (SNOM) and apertureless SNOM (photo-assisted scanning probe microscope) were developed to obtain additional information on sample surfaces.[45,46] It is based on optical-field confinement by surface plasmons of a submicron metal particle. The field extended to a nearby sample surface and was re-radiated by the particle, thereby generating a Raman, a two-photon, or a second-harmonic spectrum. In addition, SNOM and apertureless SNOM have recently aroused great interest in nanoscopy[47,48] and nanofabrication.[13,49] The concept is also applicable to submicrometer lithography and ultra-high-density optical recording.[50]

Many studies have also focused on theoretical aspect of optical near-field phenomena in terms of optical field enhancement and effect of nanoparticle, nanotip shapes. Using a small particle model, Dickmann[51] *et al.* evaluated the intensity gain versus tip aspect ratio for different tip materials at a wavelength of λ=532 nm. A maximum intensity gain of up to 10^6 could be obtained for excellent conducting metals (e.g., gold and silver). However, the estimated value was much larger than the experimental results. Using a quasistatic model, Denk and Pohl[41] presented their