

DIAMOND FILM DEPOSITION USING LASER-ASSISTED COMBUSTION  
FLAMES

by

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A DISSERTATION

Presented to the Faculty of  
The Graduate College at the University of Nebraska  
In Partial Fulfillment of Requirements  
For the Degree of Doctor of Philosophy

Major: Electrical Engineering

Under the Supervision of Professor Yongfeng Lu

Lincoln, Nebraska

December, 2014

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# DIAMOND FILM DEPOSITION USING LASER-ASSISTED COMBUSTION FLAMES

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University of Nebraska, 2014

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Due to the wide range of the superior properties, diamonds are of great interest in industry applications and scientific research. The inherent shortcomings of conventional chemical vapor deposition methods and the ever-increasing demand for diamonds urge extended efforts for further enhancement of diamond deposition without compromising the diamond quality. Conventional chemical vapor deposition processes, which rely on thermal heating, are inefficient energy coupling routes to drive gas reactions. As an intensive, coherent and monochromatic light, laser is an ideal candidate for exploring alternative energy coupling pathways. To address these challenges, the research efforts in this dissertation mainly focused on laser incorporation in combustion chemical vapor deposition of diamond films, which led to: 1) promotion of energy coupling efficiency; 2) enhancement of diamond deposition; 3) control of the crystallographic orientation; and 4) identification of active species roles in combustion chemical vapor deposition of diamond films.

Pure diamond and nitrogen-doped diamond films were deposited using combustion flames assisted by infrared-laser vibrational excitations of ethylene and ammonia molecules, respectively. Vibrational excitations of precursor molecules were realized using a kilowatt wavelength-tunable CO<sub>2</sub> laser with a spectrum range from 9.2 to

10.9  $\mu\text{m}$ . On-resonance excitation of the  $\text{CH}_2$ -wagging mode of ethylene molecules was demonstrated to be more efficient than off-resonance excitations in promoting the deposition rate and improving the diamond quality attributed to a higher energy coupling efficiency. Ro-vibrational excitations of ethylene molecules enabled crystallographic control in  $\{100\}$ -textured diamond film deposition. Micro-crystalline nitrogen-doped diamond films with a high doping concentration were deposited using an ammonia-added oxyacetylene flame assisted by infrared-laser vibrational excitations of the NH-wagging mode of ammonia molecules.

Another form of laser incorporation, a femtosecond laser induced gas breakdown, was introduced into the combustion chemical vapor deposition of diamonds as well. The diamond deposition rate was increased by a factor of 1.13 with a femtosecond laser induced gas breakdown occurred at the inner flame tip.

Optical emission spectroscopy and mass spectrometry were performed to achieve an in-depth understanding of laser effects on diamond deposition and to identify active species roles in diamond formation.

## ACKNOWLEDGEMENT

Throughout my Ph.D. studies, I have gained so much through the study here in the Department of Electrical Engineering at the University of Nebraska-Lincoln (UNL). I would like to express my sincere gratitude to all the people who have provided great help and valuable suggestions both in my academic study and personal life.

First of all, I would like to thank my supervisor, Prof. Yongfeng Lu, who provided strong support to my Ph.D. studies and gave wise advices to my life. From his help and advices, I have made great progress in my research and learned to be a responsible and confident people in life.

Secondly, special thanks go to my degree committee members, Prof. Natale J. Ianno from the Department of Electrical Engineering, Prof. Dennis R. Alexander from the Department of Electrical Engineering and Prof. Xiaocheng Zeng from the Department of Chemistry at UNL, for serving as my doctoral supervisory committee.

Thirdly, I would like to thank Drs. You Zhou and Han Chen from the Center for Biotechnology Core Research Facilities (CBCRF) at UNL for help on scanning electron microscopy (SEM). I would like to thank Prof. Mathias Schubert from the Department of Electrical Engineering for help on stylus profile.

Fourthly, I appreciate assistance and supports from my friends and colleagues in the Laser-Assisted Nano Engineering (LANE) laboratory. Specifically, Dr. Yunshen Zhou gave many wise suggestions both in research projects and in life. Drs. Zhiqiang Xie, Xiangnan He, Yang Gao, Wei Xiong, and Masoud Mahjouri-Samani taught me sample preparation and characterization techniques such as laser-assisted combustion technique,

laser-assisted chemical vapor deposition, and optical emission spectroscopy. I would also thank other members, including current and previous members in LANE laboratory: Drs. Jongbok Park, Huifu Luo, Hao Wang, Premkumar Thirugnanam, Lianbo Guo, Jin Sun, Dawei Li, Wei Qiu, Shizhen Xu, Thomas Guillemet; Mrs. Mengxiao Wang, Xi Huang, Matt Mitchell, Xu Ji, Lijia Jiang, Mengmeng Wang, Changmao Li, Hossein Rabiee Golgir, Kamran Keramatnejad, Yao Lu, and Chenfei Zhang; Mss. Ying Liu, Lei Liu, Wenjia Hou, and Yutian Lei, for their help.

Finally, I would like to convey great appreciation to my family members: including my parents, Mr. Cun Fan and Ms. Jianyun Yang, my parents-in-law, Mr Xiuja Mu and Ms. Xuehong Jia, my husband, Mr. Sai Mu, and my son, Junze Mu. Without their supports, it would have been very hard for me to get through the Ph.D.

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PREVIEW

## LIST OF ABBREVIATIONS

The following table lists abbreviations and corresponding meanings used throughout the dissertation. The page on which each one is defined or first used is also given.

Abbreviation	Meaning	Page
CVD	Chemical vapor deposition	2
CW	Continuous wave	3
C <sub>2</sub> H <sub>4</sub>	Ethylene	3
NH <sub>3</sub>	Ammonia	3
FLIGB	Femtosecond laser induced gas breakdown	3
MS	Mass spectrometry	5
HPHT	High-pressure high-temperature	11
HF	Hot-gas breakdown	14
DC	Direct-current	14
RF	Radio-frequency	14
MP	Microwave plasma	15
C <sub>2</sub> H <sub>2</sub>	Acetylene	15
C <sub>3</sub> H <sub>8</sub>	Propylene	15
CH <sub>4</sub>	Methane	15
IR	Infrared	19
LCVD	Laser-assisted chemical vapor deposition	21
WC	Tungsten carbide	42
SEM	Scanning electron microscopy	43
OES	Optical emission spectroscopy	47
IVR	Intramolecular vibrational relaxation	52
slm	Standard liters per minute	54
O <sub>2</sub>	Oxygen	54
sccm	Standard cubic centimeters per minute	97

# CHAPTER 1 INTRODUCTION

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## 1.1 Motivations

## 1.2 Dissertation outline

## 1.3 References

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PREVIEW

## 1.1 Motivations

The ultimate purpose of chemistry is obtaining anticipated outcomes through precisely designed precursors and reactions [1-4]. Therefore, it is highly important to steer reaction pathways by either dynamic, varying external parameters (such as temperature, pressure and concentration), or kinetic approaches, introducing a catalyst which selectively lowers the activation barrier to a particular reaction channel [2, 5]. Laser provides a powerful tool in steering chemical reaction dynamics and kinetics [6]. A laser chemical reaction is generally a cold-wall process, in which laser energy is selectively deposited into reactant molecules. Depending on how the laser energy is coupled, the influence of the laser irradiation can be either dynamic, equilibrium thermal heating, or kinetic, selective activation of specific molecules via vibrational or electronic excitation above a particular reaction barrier towards a certain reaction channel. Investigations on how laser irradiation affects the chemical reactions are still limited to a lab-bench scale without field-scale studies.

Due to the wide range of the extreme properties, diamonds are of great interest in industry applications, including optical windows, heat spreaders, electro-chemical detectors, radiation sensors and high-power high-temperature electronics [7-10]. At present time, chemical-vapor-deposition (CVD) diamonds dominate the synthetic diamond market. The inherent shortcomings of conventional CVD methods and the ever-increasing demand for diamonds urge extended efforts for further enhancement of diamond deposition without compromising the diamond quality. Conventional CVD methods generally require a high temperature to overcome the energy barrier [11-14], which are inefficient energy coupling routes to drive gas reactions. Attempts on selective

promotion of diamond growth have been made by deploying the unique properties of lasers, including monochromaticity, coherence and directionality. J.H.D. Rebello *et al.* reported a successful synthesis of diamonds by pumping CO molecules to high vibrational states using a continuous wave (CW) CO laser operating on its low vibrational transitions [15]. Z. Toth *et al.* used a Nd:YAG laser (1064 nm) in a perpendicular irradiation geometry to achieve localized diamond deposition in the beam covered region [16]. However, the low growth rates make these approaches impractical for scalable production.

In the research described in this dissertation, efforts were extended to enhance the diamond growth, to control crystallographic orientations, and to investigate the laser effects on the flame chemistry and diamond growth. The research projects mainly focused on the following five tasks: 1) diamond deposition using combustion flames assisted by on- and off-resonance vibrational excitations of ethylene ( $C_2H_4$ ) molecules; 2) controlled growth of {100}-textured diamond films using combustion flames assisted by ro-vibrational excitations of  $C_2H_4$  molecules; 3) micro-crystalline nitrogen-doped diamond film deposition with laser resonant vibrational excitations of ammonia ( $NH_3$ ) molecules; 4) diamond deposition using combustion flames assisted by a femtosecond laser induced gas breakdown (FLIGB); and 5) investigation of active chemical species roles in the diamond growth.

## 1.2 Dissertation outline

This dissertation focused on enhancing the diamond growth, controlling the crystallographic orientation of the diamond deposition, exploring alternative efficient

energy coupling paths and understanding the diamond growth mechanism. The whole dissertation is divided into nine chapters. Chapter 1 introduces the motivation and outline of this dissertation. Chapter 2 reviews the background of diamond, diamond synthesis, laser chemistry and laser-assisted material synthesis. Chapter 3 describes the experimental methods adopted in the study, including the sample preparation procedure, diamond film characterizations, and combustion flame diagnostics. Chapter 4 demonstrates the laser-assisted vibrational excitations of  $C_2H_4$  molecules for promoting the diamond deposition rate and improving the diamond quality. The  $CH_2$ -wagging mode ( $\nu_7$ ,  $949.3\text{ cm}^{-1}$  or  $10.534\text{ }\mu\text{m}$ ) of  $C_2H_4$  has a strong infrared activity and matches one  $CO_2$  laser emission line ( $10.532\text{ }\mu\text{m}$ ). Through gradually tuning the laser wavelengths centered the resonant wavelength of  $10.532\text{ }\mu\text{m}$ , on- and off-resonance excitations of  $C_2H_4$  molecules were achieved. The deposition rate was enhanced by a factor of 5.7 with on-resonance vibration excitation of the  $CH_2$ -wagging mode. On-resonance vibrational excitation was demonstrated more efficiently than off-resonance excitations in activating the  $C_2H_4$  molecules, enhancing the flame temperature and consequently promoting the diamond growth even with the same amount of absorbed laser energy. Chapter 5 describes a novel strategy to realize controlled growth of  $\{100\}$ -textured diamond films via laser ro-vibrational excitations of  $C_2H_4$  molecules. With the laser wavelength was tuned between on- and off-resonance wavelengths, the  $\{100\}$ -facet coverage rate could be finely controlled. Chapter 6 demonstrates the crystallinity of nitrogen-doped diamond films deposited using an  $NH_3$ -added oxyacetylene flame was significantly improved by laser-assisted vibrational excitations of  $NH_3$  molecules. The high nitrogen doping concentration demonstrated the potential of growing nitrogen-doped diamond films with

laser-assisted vibrational excitation of  $\text{NH}_3$  molecules. Chapter 7 studies the effects of a FLIGB on the combustion CVD of diamond films. The deposition rate was increased by a factor of 1.13 associated with an improved diamond quality with a FLIGB at the inner flame tip region, suggesting the possibility of exploiting the potential of the FLIGB in material synthesis. Chapter 8 illustrates an investigation of active chemical species roles in the combustion diamond deposition using mass spectrometry (MS). A proper ratio balance between the etchants and hydrocarbon-related species was required for high-quality diamond deposition. Chapter 9 concludes the projects with important results and suggests future research directions.

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