

Preparation and Saturable Absorption Property of Graphene on the Optic Fiber Side by Transferring CVD- Graphene Grown on Ni

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Abstract. A key enabler in the mode-locked fiber lasers has been the discovery of novel saturable absorbers (SA) such as carbon nanotubes (CNT) and graphene. We demonstrate chemical vapor deposition (CVD)-graphene on nickel (Ni) transferred onto optical fibers preserves its nonlinearity. The influence of the temperature on the growth of graphene was explored by Raman spectra, scanning electron microscope (SEM) and atomic force microscope (AFM), respectively. The results show the temperature will affect the thickness and surface uniformity of graphene on Ni film. Besides, the mechanism of CVD process and the saturable absorption property of the graphene are illustrated, respectively.

1. Introduction

Graphene is a single layer of carbon atoms arranged in two-dimensional honeycomb crystal lattice, and has been attracting significant attention due to its distinct mechanical, structural, electrical, and chemical properties, which make it promising in fields of electronics, sensing, and optoelectronics devices. One application of graphene is acting as a saturable absorber, which was firstly demonstrated in 2009. [1] When the light irradiates on graphene, graphene shows a nonlinear absorption to it, which is attributed to the SA mechanism. Graphene is believed to be an excellent SA material, due to the unique energy band gap structure with advantages of low absorption intensity, deep modulation depth, high damage threshold, fast recovery time and wide range of saturable absorption (300-2500 nm). Typically, there are three different structures of saturable absorber device, sandwich structure, evanescent wave coupling structure and waveguide-incorporated structure, realized by various methods. For example, Sun et al. [2] and Bao et al. [3] applied evaporated graphene-PVA composite and CVD-graphene in mode-locked ultrafast laser of sandwich structure, respectively. In 2015, Azooz et al. used the graphene oxide in mode-locked thulium ytterbium co-doped fiber laser [4]; and Zhao et al. use graphene film as saturable absorber for an Optical Modulator in Pulsed Laser Generation [5] in 2015.

In this paper, we demonstrate the influence of temperature on CVD-graphene growth on Ni film. The influence of the temperature on the growth of graphene was explored by Raman spectra, scanning electron microscope (SEM) and atomic force microscope (AFM), respectively. Besides, the transmission curve of the CVD-grown graphene is measured, and the mechanism of CVD process and the saturable absorption property of the graphene are illustrated.

2. Experimental



2.1. Materials and apparatus.

Ethyl alcohol, acetone, nitric acid, Ferric chloride, phosphoric acid and poly (methyl methacrylate) (PMMA) were purchased from Sigma-Aldrich Shanghai (Shanghai, China). Vacuum pump used in this experiment was from Woosung Vacuum Co. Gas Mixing System used in this experiment was from MTI Corporation. Mini tube furnace was from Thermcraft.

2.2. Preparation of Graphene.

The graphene was synthesized by a laboratory-built ultralow-pressure thermal CVD system with a quartz tube furnace. CH_4 served as the carbon source and Ni film as the catalyst. The Ni film was placed on a quartz plate and then loaded into the center of the quartz tube furnace. After the pressure decreased below 20 mTorr by air pump, then Ar, methane, hydrogen was injected until the gas detection circuit became normal. The preparation process included heating, annealing, growth and cooling with different temperatures shown in figure 1. Firstly, the reactor was heated to the pretreatment temperature. Annealing is the first chemical reaction process of the whole process, to clean and chemically modify the surface of Ni, and optimize its crystallinity, roughness and grain size as much as possible for the subsequent steps of the growth of graphene.

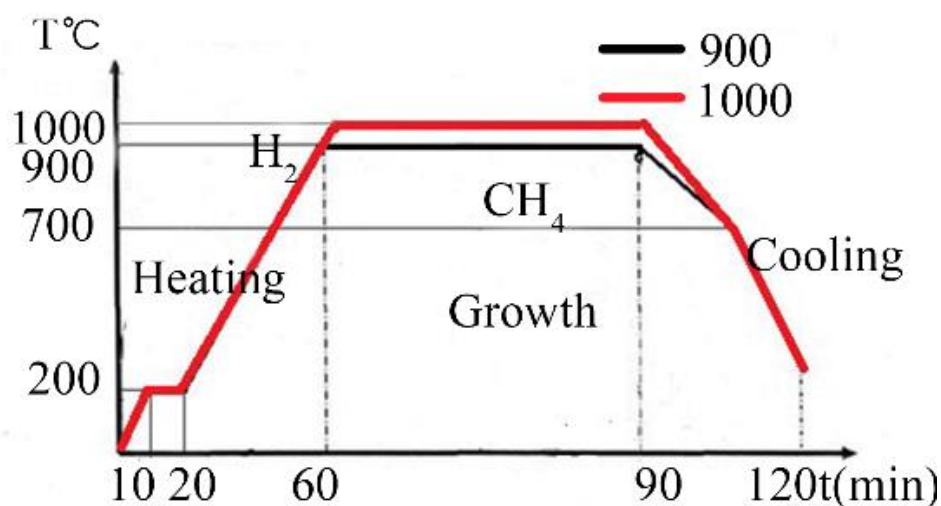


Figure 1. Temperature changes through the preparation of graphene.

2.3. Transfer of graphene to the optical fiber side.

PMMA was spin coated onto the graphene on the Ni film, followed by heating at 150 °C for 10 min. Then the sample was immersed in ferric chloride and deionized water to dissolve the Ni film and remove the residual ferric chloride, respectively. After transferred onto the optical fiber side, the PMMA/graphene was heated at 150 °C for 10 min to gain a good contact between graphene and the optical fiber. Finally, the fiber side was immersed in acetone to dissolve the PMMA, and thoroughly rinsed.

2.4. Measurement of the graphene absorber.

We tested the saturable absorption property of the graphene SA with a laser diode at 473 nm as the input light source. The measured transmission experimental apparatus of the prepared graphene SA is shown in figure 2. The light intensity at both ends of the optical fiber is measured by optical power meter. With the increase of light intensity, the increase of transmittance rate is decreased gradually, even invariant.

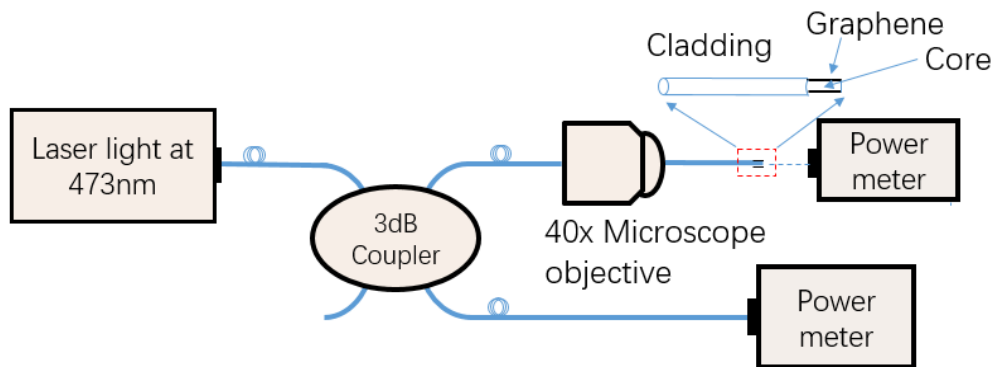


Figure 2. The measured transmission schematic diagram of the prepared graphene SA.

3. Results and discussions

3.1. Raman spectrum graphene.

The Raman spectra of the samples synthesized on Ni film at temperature of 900 °C and 1000 °C are shown in figure 3. The two most intense features are the G peak at ~1580 cm⁻¹ and a band at ~2680 cm⁻¹, historically named 2D, since it is the second most prominent peak in graphene samples. The G peak is due to the doubly degenerate zone center E_{2g} mode. And the 2D peak is caused by two reverse momentum of the carbon atoms in double phonon resonance transition, its movement and shape is closely related to graphene's layers. The G peak and 2D peak indicate the existence of graphene, and the absence of D and G' peaks prove that there is no disorder of graphene. [6] The ratio between the intensity of 2D peak and G peak (I_{2D}/I_G) is relative to the number of graphene layers. It is clear that I_{2D}/I_G is about 1.2 at 900 °C and I_{2D}/I_G is about 0.64 at 1000 °C in figure 3. Therefore, that the thickness of CVD-graphene film at 900 °C is thinner than that at 1000 °C.

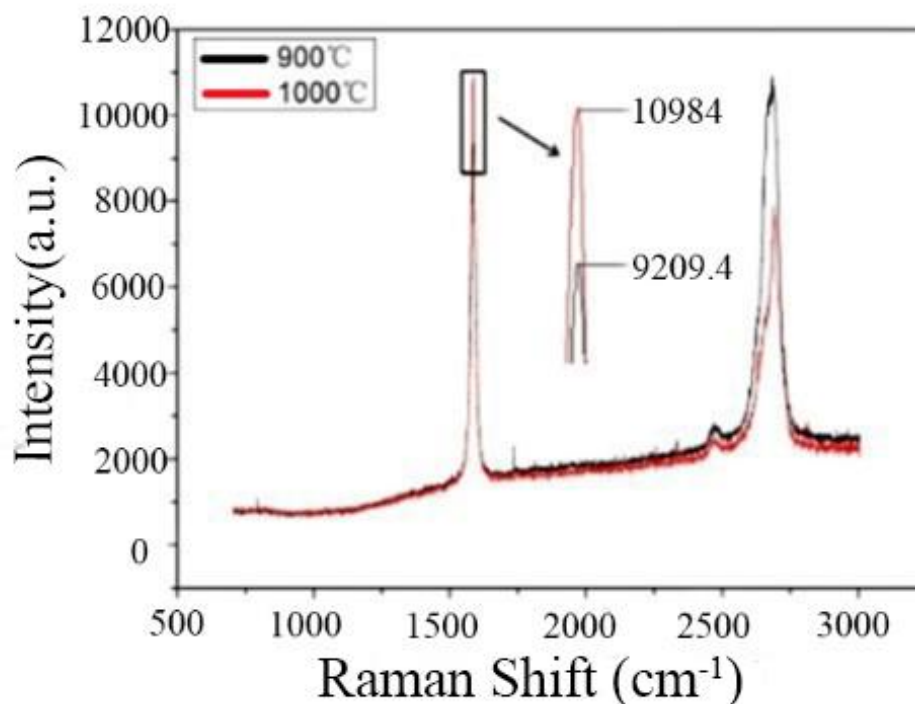


Figure 3. Raman spectra of graphene grown at 1000 °C (a) and 900 °C (b), respectively.

3.2. SEM images of graphene.

The SEM images of CVD-grown graphene at 900 °C and 1000 °C are shown in figure 4(a) and (b), respectively. The graphene film grown at 900 °C has good continuity and uniformity, while the graphene film grown at 1000 °C has many folds and some nanoplatelets graphene agglomeration. It is because the graphene growth on Ni is a deposition-segregation process (figure 4.c) [7]; ^{12}C and ^{13}C graphene pattern grown on the Cu film are separated, while on the Ni, they are evenly distributed. This indicated that graphene growth on Ni is deposition-segregation mechanism, while growth on Cu is a surface process. And the carbon solubility of nickel increases with the temperature increasing, so the carbon atoms agglomerate into graphene folds.

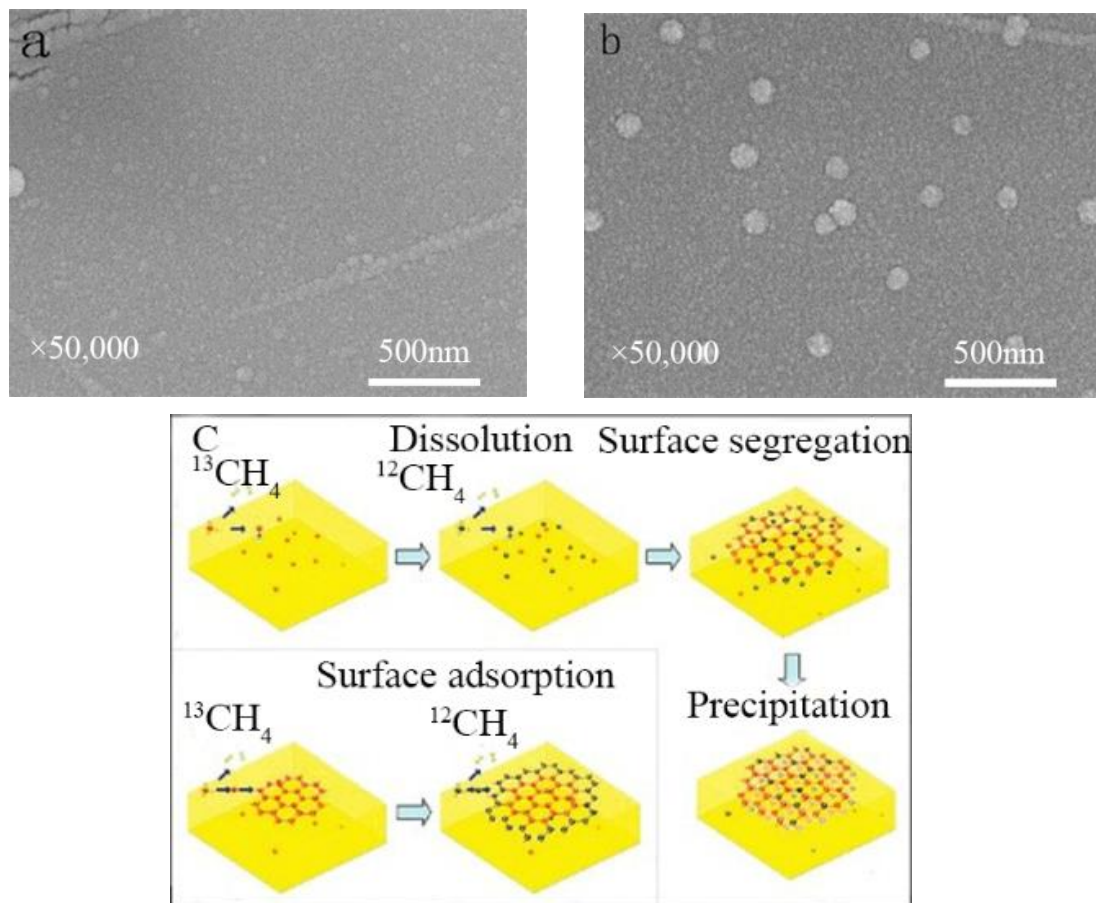


Figure 4. SEM of graphene prepared at 900 °C (a) and 1000 °C (b), respectively. (c) The mechanism schematic diagram of deposition and surface precipitation in the process of growth of graphene.

3.3. AFM images of graphene.

It is evident that the graphene film is roughly uniform in the AFM images as shown in figure.5. It can be seen that the thickness distribution of the graphene film is around 36 nm, except for a few folds of 174 nm. The thickness of single layer graphene is theoretically 0.334 nm [8], but experimentally 0.7~1.2 nm due to the surface absorption-caused change of carbon atom's van der Waals radius. Therefore, the number of graphene layers is about 30 layers. From the results by SEM and AFM, we can see that the CVD-graphene film grown at 900 °C has better continuity and uniformity than that at 1000 °C.

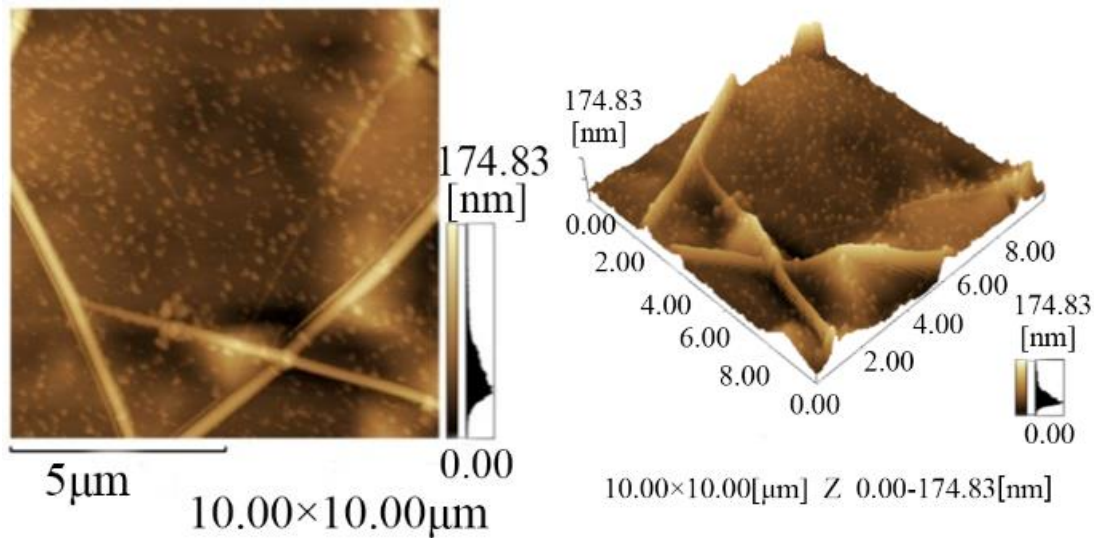


Figure 5. AFM images of graphene growth on 900 °C

3.4. Graphene absorber experiment.

The measured transmission curve of the optical decorated graphene in side SA is shown in figure 6. The modulation depth is ~9.5% and the nonsaturable loss is ~50%. Note that the modulation depth is dependent on the amount of graphene layer on the fiber side [9]. The nonsaturable loss is less than the other article (~63.1%) [10].

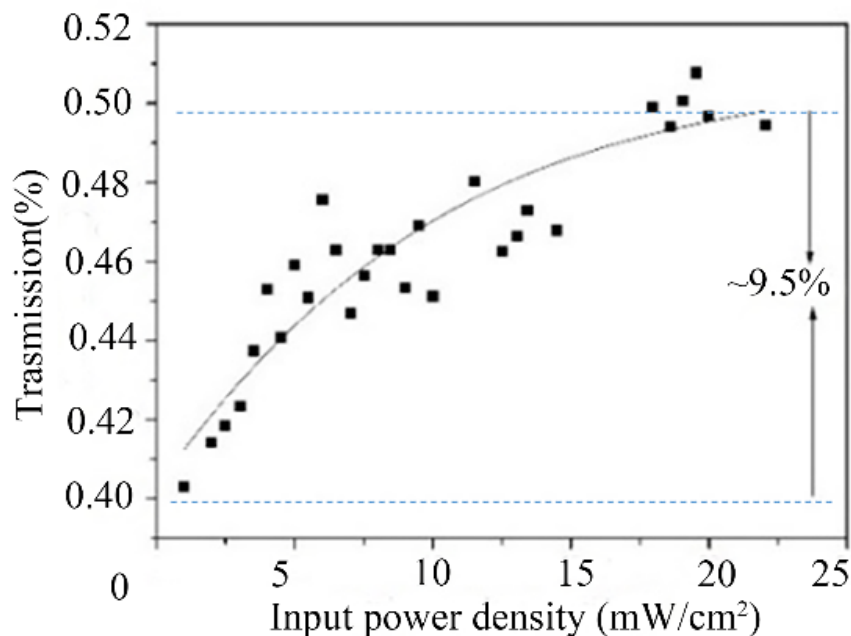


Figure 6. Transmission curve of graphene SA.

4. Conclusion

In this paper, it was found that the number of graphene layers is controllable via modulating the reaction temperature of the CVD process on Ni film. The results show that the CVD-graphene at 900 °C on Ni film has better uniformity than that at 1000 °C. The modulation depth of the CVD-graphene SA is 8% and the nonculturable loss is 50%, which indicating a promising prospect in mode-locked laser.

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Acknowledgments

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