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STUDY OF HEAT DISSIPATING MATERIAL USING BORON NITRIDE FABRICATED BY LASER ABLATION

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Abstract. More research interest is developing rapidly on two dimensional (2D) materials owing to their excellent electro-optic properties to develop next generation of electronics and highly functional devices. Among well-known and widely used 2D materials, boron nitride (BN) is an electrical insulator with a band gap of 5.5 eV, and attests high chemical stability, outstanding mechanical properties, and high thermal conductivity. Accordingly, BN is considered as a promising candidate to improve the heat dissipation material performance. In this study, the cooling rate of composite materials of poly methyl methacrylate (PMMA), hexagonal boron nitride (h-BN) and gold nanoparticles was investigated using femtosecond transient absorption spectroscopy. The main objective of this study is to prepare the flexible BN-PMMA films could have a significant impact on heat dissipation to enhance the performance of electronics devices. BN nanostructures were prepared by nanosecond laser ablation in acetone. The laser ablation was carried out at room temperature with laser ablation time of 120 min. The SEM images of bulk BN and laser ablated BN were obtained for structural and surface morphological characterization. Gold colloidal solution was prepared using gold nano-particles with chloroauric acid and distilled water. For the preparation of composite film, PMMA was dissolved in acetone solvent and then mixed with BN and gold colloid solution. The prepared composite films were examined for cooling rate of photoexcited gold nanoparticles using femtosecond transient absorption spectroscopy. It is found that the lifetime is shorter for composite films with Au and high BN content.

Keywords: boron nitride, laser ablation, X-ray diffraction, raman spectroscopy, scanning electron microscopy, cooling process, transient absorption spectroscopy (TAS)

1. Introduction

During the past few years, (2D) materials have received a great deal of interest due to their wide application in micro and nano optoelectronics, photocatalysis and energy conversion device. Significant progress has been achieved in preparation of 2D materials using various synthesis methods such as mechanical exfoliation, chemical exfoliation and hydrothermal or solvothermal reactions, and chemical vapor deposition. These techniques are very effective to fabricate high quality nanosheets with limited efficiency [1-3]. A widely used 2D form of carbon is called as graphene. Graphene is well-known and one of the most extensively studied materials because of its fascinating physical and chemical properties [4-6]. It can be exfoliated from graphite. Graphite, a base material for graphene, is relatively low cost and widely used in our daily life such as lead of pencil. In the same way, besides graphene, atomically thin transition-metal dichalcogenides (TMDs) also attracts enormous attention all over the world [7]. TMDs layered materials such as Molybdenum sulfide (MoS_2), Tungsten

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sulfide (WS_2) and Boron nitride (BN) exhibits unique features and characteristics, establishing their significance in opto-electronic devices and applications. BN nanostructure has greatly shown its potentials for applications in high performance devices like electron devices, gas absorbents and reinforcing agents [8]. BN can be found in two forms; hexagonal BN (h-BN) and cubic BN (c-BN). Among these, h-BN having similar structure to graphite is new material for research as compared to widely studied c-BN. The h-BN is now widely used in study. Recently, success in synthesis of Boron nitride nanotube (BNNT) has gaining much attention because of their physicochemical properties. BNNT has similar nanostructure to that of carbon nanotube (CNT) where boron and nitrogen atoms are arranged in hexagonal network. BNNT displays comparable or even better characteristics as compared to CNT and is considered as a promising material for strengthening polymers, ceramics and metals because of it has high rigidity and high chemical stability. It also exhibits superior properties like antioxidant power and heat resistance, it is hard to oxidize up to 950^{o}C and structurally stable up to 900^{o}C. It is reported that the h-BN can change to BNNTS and C-BN by using laser ablation [2]. In the last decade, there have been few reports on the alternative routes for the preparation of BN using the polymer as a precursor. In this context, few reports suggest that poly methyl methacrylate (PMMA) and poly-styrene (PS) can be used as precursor to synthesis BN-polymer composite film [3]. When BN coated with polymer, it shows improvement in the properties such as thermal conductivity and mechanical strength due to the interfacial adhesion in the composite films. Furthermore, previous reports suggest that the fabrication of new functional material combined with 2D materials and metal nanoparticle. The formation of new composite materials exhibits superior performance as compared to noble metal nanoparticle because of excellent characteristic of 2D material, the obtained large surface area, chemical stability and prevention of aggregation of nanoparticles. Also, composite material of graphene and gold nanoparticle is emerging as a material with future potential for high sensitivity electrochemical sensor [9-10]. In addition, composite material like Au nanoparticle modified with of MoS_2 nanostructure can be possible serve as an active substrate to produce enhanced light absorption [11]. Most recently, advancement in information and communication technologies accelerates the research activities for the production of innovative machines and devices. This creates increase in the demands of electronic parts such as CPU and memory. For the development of flexible electronic devices, a flexible material with superior heat dissipation are needed around the world [12]. The heat released from smaller electronic devices could alter the performance which results in overheat or explosion. The heat dissipation is one factor which limits to develop electronic devices such as mobile phones and batteries. Since BN produces high thermal conductivity, it can be effectively used to control heat dissipation. Therefore, it is thought that BN could be considered as promising material to control heat dissipation to make smaller devices cooler and safer without causing damage.In the present work, we have prepared composite film of BN with flexible PMMA and Au nanoparticle. The cooling process of BN and polymer composite films were studied using femtosecond transient absorption spectroscopy.

2. Experimental

Chemicals and Materials. Chemicals and materials used were purchased and used as received; BN powder (Wako Chemical Japan), $HAuCl_4$ $4H_2O$ (0.1 ml 2.5×10^{-5} mol) (Kishida Chemical, Japan, 99.0 %), $Na_3C_6H_5O_7$ (Kanto Chemical, Japan: 0.100 g /10 ml, 294.1 g /mol), Poly-metylmetaclyl-acid (PMMA), Acetone (Kishida Chemical, Japan: 99.5%)

Preparation of 40 nm diameter gold nanoparticles by chemical synthesis. Gold nanoparticles are synthesized by the chemical method. $HAuCl_4$ aqueous solution (0.1 ml: 2.5×10^{-5} mol) was added into deionized water (100 ml). The mixture was heated and stirred at 100ºC. Then, the $Na_3C_6H_5O_7$ (1 ml) solution was added into the mixture. After the

mixture was stirred at heating for 5 minutes and then kept for cooling at room temperature. Finally, deionized water was added for total volume 100 ml. Au nanoparticle size was determined by the experimentally observed peak position from UV-vis spectra.

Preparation of PMMA–Au–BN nanocomposite. PMMA solution was prepared as follows: 4 g of PMMA (M_w = 100,000) was dissolved into 30 ml of Acetone. After this, 1 mg and 5 mg laser ablated BN powder was added into PMMA mixture and stirred for 10 minutes to prepare PMMA-Au-BN solution. Then, PMMA solution was mixed with 13 ml of Au nanoparticle colloid. PMMA-Au-BN nanocomposite film was prepared transferring. PMMA-Au-BN solution on glass substrate at room temperature for 3 hours. The PMMA-Au-BN composite film with 1 g of BN and 5 g of BN hereafter referred as sample 1 and sample 2 respectively. The preparation details of sample 1 and 2 is shown in Table 1.

Table 1. Synthesis of BN, PMMA and Au Colloid

Sample	BN (mg)	Au (nm)	BN:Au (Weight ratio)
S1	1	40	16:1
S2	5	40	78:1

Laser Ablation and characterization. The BN nanoparticle was prepared by nanosecond laser ablation using acetone as a solvent. We used analytical grade h-BN powder about 100 mg mixed with 30 mL acetone into a glass bottle. The solution was kept under magnetic stirring for 30 min prior to laser ablation. The laser ablation was carried out with Nd:YAG laser (wavelength 532 nm, pulse duration 10 ns, pulse repetition frequency 10 Hz, beam size 5 mm and laser power 56 mJ). During the laser ablation process, the solution was rotated by magnetic stirrer and laser ablation time was 120 min. After laser ablation, BN colloidal suspension was heated in air to obtain dry BN nanoparticle in the form of powder. The laser ablated BN nanoparticles sample was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm the formation of nanostructure, surface morphological changes as well as structural features.

Transient Absorption Spectroscopy (TAS) using femtosecond laser (cooling process of Au nanoparticle). Cooling process of the PMMA-Au-BN film was investigated using femtosecond transient absorption spectroscopy. The measurements were carried out with an amplified Ti:sapphire laser (800 nm wavelength, 130 fs fwhm pulse width, 0.8 mJ/pulse intensity, 1 kHz repetition; Spectra Physics, Hurricane). The second harmonic of 400 nm wavelength at a 500 Hz modulation frequency was used for a pump light. On the other hand, the white-light continuum generated by focusing the fundamental beam from Ti:sapphire laser onto a sapphire plate (2 mm thick) was used for a probe light. The probe light was focused at the center of the pump light (~0.3 mm diameter) on the sample, and the diffuse reflected probe light was detected by a Si photodiode after passing through a monochromator (Acton Research, SpectraPro-150). Au nanoparticle of dispersion including PMMA film was irradiated by the pump light (400 nm). Cooling effect of PMMA film including BN was measured by probe light (850 nm).

3. Results and discussion

The spectroscopic data of bulk BN and laser treated BN were obtained using XRD diffraction, Raman spectroscopy and SEM. Figures 1(a) and 1(b) display the XRD spectra of bulk BN powder and laser-treated BN for 120 min. Figure 1(a) shows that the intensity of the diffraction peak (002) and (004) decreased for laser-treated BN with small shift as compared to the bulk BN. It suggests that the bulk BN has been transformed into h-BN nanostructure after the laser ablation while keeping its crystalline structure unchanged [13]. Figure 1(b)

shows that the intensity of the diffraction peaks (101), (100) and (102) slightly increases. It indicates that the c-BN content is also observed after laser ablation.

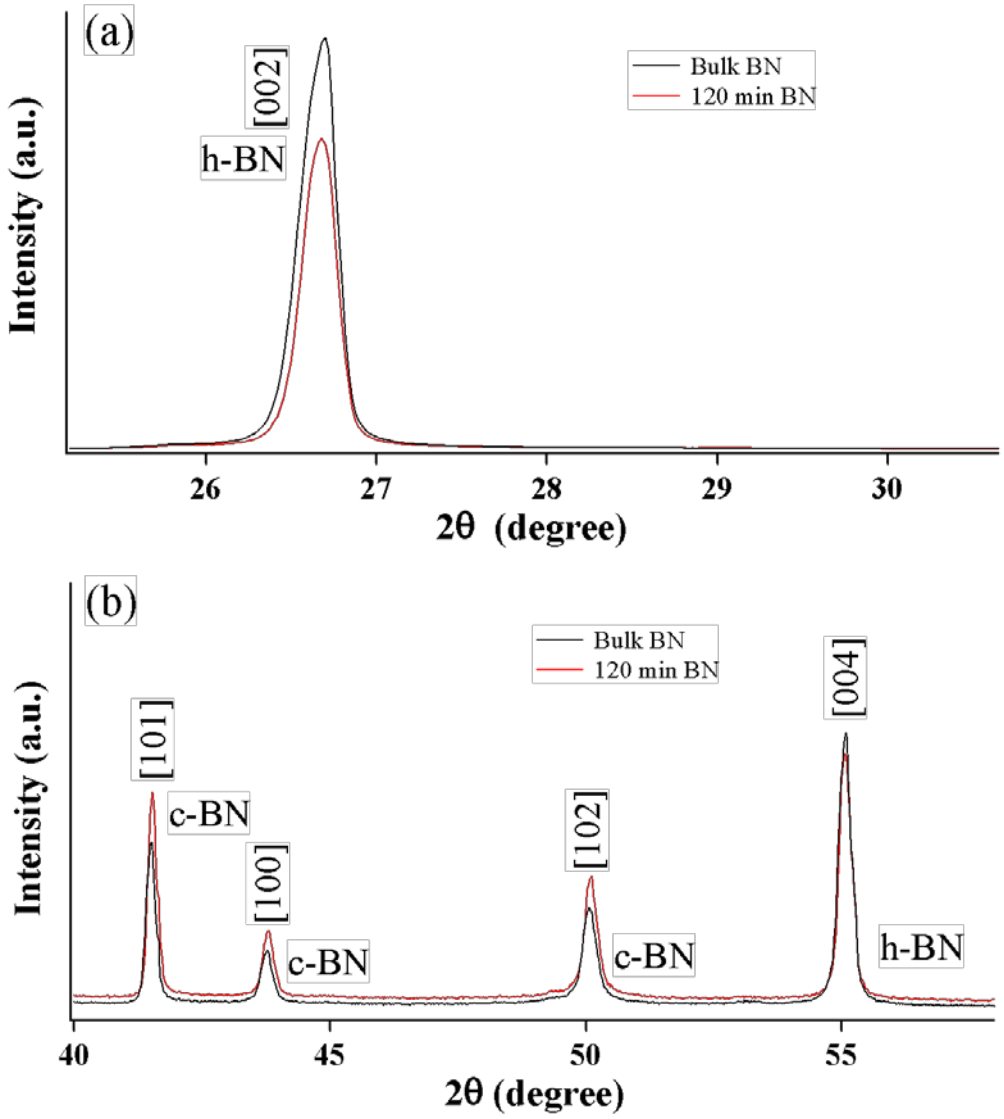

Fig. 1. High resolution XRD spectra of (a) bulk BN powder and (b) laser ablated BN

The raman spectra of bulk BN powder and laser-treated BN for 120 is shown in Fig. 2. In case of laser ablated BN, the spectra graph indicates that the signature peak assigned to h-BN is observed at 1364.4 cm^{-1} [7,14]. The increase in the intensity of peak at 1364.4 cm^{-1} confirms that h-BN nanostructure was still unchanged after the laser ablation.

Figure 3 illustrates SEM images of bulk BN powder and laser ablated BN for 120 min. The SEM images show the formation of BN nanostructures upon laser ablation. Figure 3 (a) shows that the BN sheets having the diameter varies from 2 µm to 10 µm. In the case of laser ablated BN sample, the formation of nanoparticle is observed with diameter of 30-70 nm and the transformation of bulk BN powder into BN nanostructure might be due to the intense thermal activity produced during laser ablation.

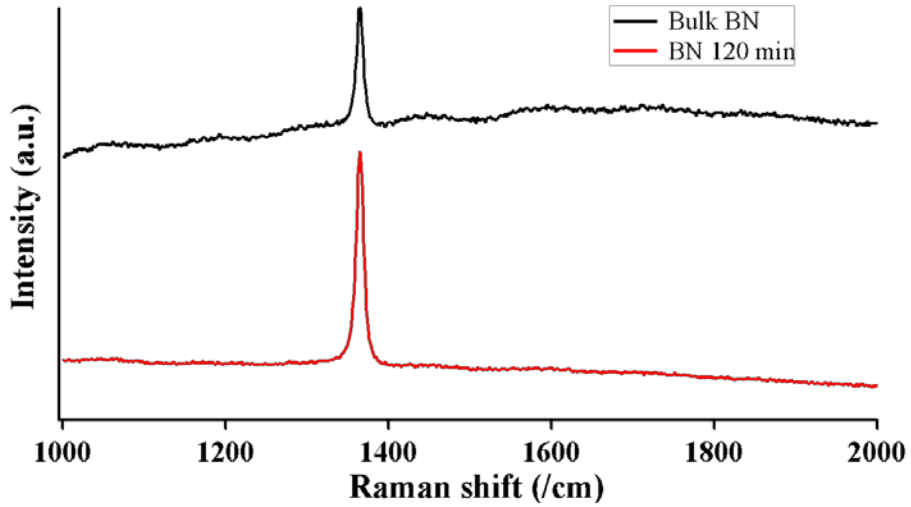

Fig. 2. Raman spectra of laser ablated BN

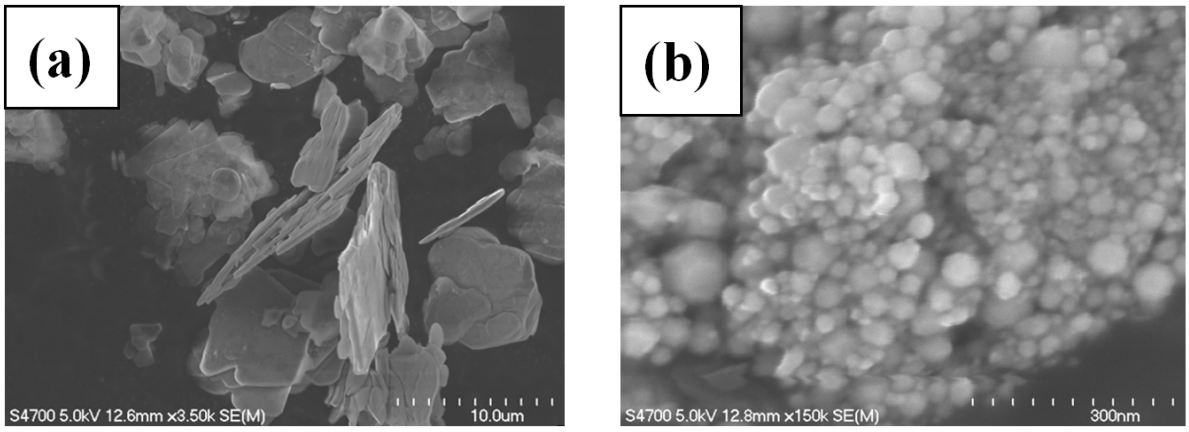

Fig. 3. SEM images of (a) Bulk BN, (b) 120 min laser ablated BN

Figure 4 shows the UV-vis reflection spectra results of PMMA film, sample S1 and sample S2. The reflectances of sample S1 and sample S2 are noticeably lower around 550 to 570 nm, extending toward longer wavelength around 800 nm as compared to the nearly constant reflectance of PMMA film. This lowering in the reflectance might be attributed to aggregation of Au nanoparticle in sample S1 and sample S2, because non-aggregated Au nanoparticles could not show such a broad absorption band.

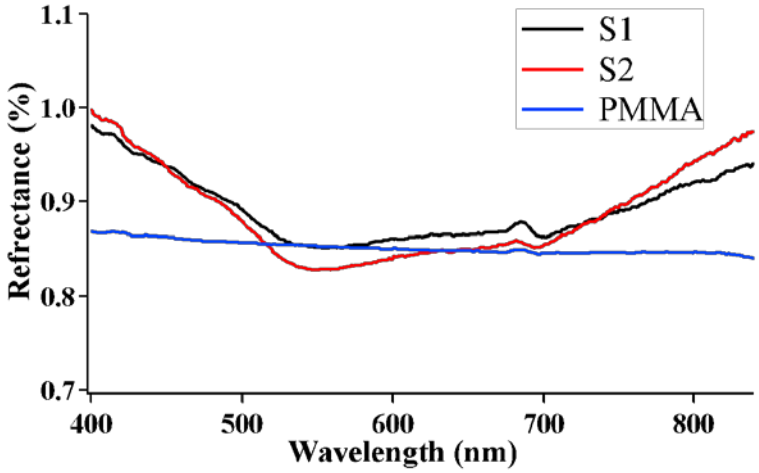

Fig. 4. Reflection spectra images of PMMA and Au-BN-PMMA composite films

Figure 5 shows that transient absorption spectroscopy (TAS) using femto second laser (Probe light: 850 nm, Excitation light intensity: 3.0 mW). The summery of sample lifetime is shown in Table 2 from TAS measurement fitting graph result.

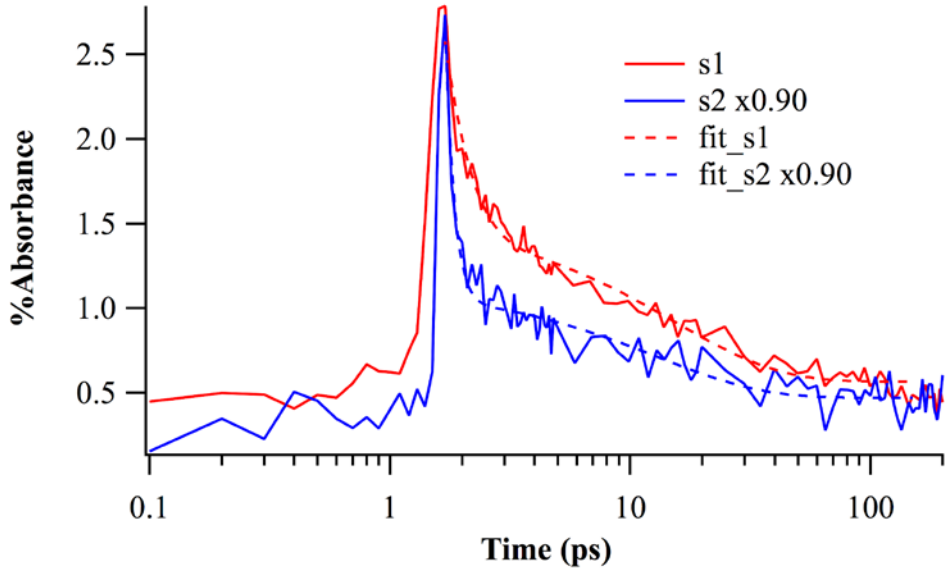

Fig. 5. TAS measurement of PMMA films including BN and Au

Cooling process of Au nanoparticle by photoexcitation was observed as reported previously [15]. 400 nm excitation generates electron-hole pairs in the Au nanoparticle and electron-electron scattering elevates the electron temperature within 100 fs. Thermal equilibrium process happens by electron phonon scattering of the internal Au nanoparticle from 100 fs to 1 ps. Thermal diffusion process happens by Au phonon – media phonon scattering from 10 ps to 100 ps. It is seen that heat transfer occurs from Au nanoparticle to circumference medium.

Table 2. Sumary of lifetime of sample S1 and S2

Sample	tau 1	tau 2
S1	0.45591 ± 0.0504	15.396 ± 1.6
S2	0.15535 ± 0.0186	13.064 ± 2.23

Long wavelength area of plasmon band became broader by photoexcitation and the effect was observed in this transient absorption experiment of using probe light of 850 nm. Here the growth and decay of the transient signals correspond to temperature increase and decrease. Figure 4 shows that sample including low BN (sample S1) has long lifetime better than sample including more BN (sample S2) (see tau 2 vales in Table 2). That is, cooling process of Au nanoparticle after photoexcitation of including more BN is promoted by the effect of efficient heat transfer property of BN.

4. Conclusions

We have successfully prepared the BN nanostructures using nanosecond laser ablation in acetone. The formation of BN nanostructure was confirmed by XRD, raman spectroscopy and SEM measurements. We prepared to PMMA composite films with the laser ablated BN and Au nanoparticle of a 40 nm diameter. The cooling process after exciting the Au nanoparticles in the film was examined using femtosecond transient absorption spectroscopy and the effect of BN as an efficient heat dissipater was observed. Heat dissipation performance from BN

could play a crucial role in energy saving and enhance the overall performance of electronic devices. Therefore, it is recommended that further research on heat dissipation is important to resolve a major challenge of high-temperature rise during the process which reduces the efficiency of future generation flexible electronic devices.

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