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Probing ultrafast dynamics of photo-excited Bismuth nanostructure

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Abstract

The present work shows the primarily results of ultrafast dynamics of photo-excited Bismuth (Bi) nanostructure through Femtosecond optical pump-probe spectroscopy technique. The study is an attempt to explore distinctive features of Bi nanostructure manifested due to its unusual electronic properties. The results reveal Bismuth charge carrier dynamics in terms of positive ΔA/A signal in visible-NIR region due to photo-excitation of Bi nanostructure by ultrafast pulses. The positive signal is attributed to excited state absorption arises due to various reasons like surface plasmons and phonons in visible region and interband plasmonic resonances in NIR region. The observed features of ultrafast dynamics reflect potential of Bi for applications of solar energy harversting.

1. Introduction

Bismuth (Bi) being a groupV semi-metal has motivated and attracted anormous attention from scientific community due to its anomalous properties like diamagnetism, superconductivity and lowest thermal conductivity among metals. It is a good thermoelectric material [1] which shows substantial high thermoelectric coefficients and also exhibit plasmonic [2] and photocatalytic properties [3]. It also persist strong Plasmon-electron coupling, known as Plasmaron which has been observed only in graphene and elemental Bismuth. Recently, Bi is becoming appealing for the applications involving its peculiar optical properties. Especially, the researchers are highly interested to subwavelength Bi nanostructures that show a potential for supporting optical resonances in a broad spectral region and are appealing for applications in nanophotonics, plasmonics, and even metamaterial engineering. Due to its dynamic electronic and optical properties, its study has remained an interesting area of research so far.

The present work is an attempt to study dynamic features of grown Bi nanostructure utilizing ultrafast spectroscopy. It manifests structural and optical properties of Bismuth nanostructure grown directly on Si (001) without any buffer layer. However, Bi based compounds like bismuth-antimonide and bismuth-selenide had been studied for the past many decades, but ultrafast charge carrier dynamics of elemental Bi needs more attention. Femtosecond optical pump-probe experiments performed with bismuth so far generally focused upon detection of coherent phonons, treating electronic response only as a background. However, detailed information of ultrafast electronic dynamics of bismuth is needed to explore the use of this material for various applications of solar energy. Here we report ultrafast transient absorption study to explore photo-excited charge carrier dynamics and capture its photoinduced response in the visible-NIR region.

2. Experimental Methods

The bismuth polycrystalline film with self-assembled nano-clusters was prepared by physical vapor deposition on clean reconstructed Si (001) surface. The substrate cleaning followed by Bismuth growth was performed in an Ultra High Vacuum System (Varian VT-112) with the base pressure of 5 X 10^{-10} Torr. Firstly, bismuth was grown on Si at room temperature and then annealed at 410 ^{0}C to reconstruct grown Bi nanostructured film. FESEM (Field Emission Scanning Electron Microscope) images were recorded to see morphological changes, while the photoexcited charge carrier dynamics were probed using Ultrafast Femtosecond Transient Absorption Spectroscopy (UFTS) which manifest the dynamics of photo-induced electronic excitations along with its decay profile. Femtosecond pulses of wavelength 800nm with 35fs pulse width at 1 KHz repetition rate delivered from Ti:Sapphire femtosecond laser system acting as probe pulses after passing through Sapphire crystal generating white light continuum. The pump pulses were obtained from Operational Parametric Amplifier and its power density was controlled by a neutral density filter to prevent any damage to the sample. The transient absorption change ΔA/A was recorded for visible as well as NIR region.

3. Results and discussion

Figure 1(a) shows FESEM image which clearly depicts the formation of Bi nanostructure. The sample annealing

has drawn pollycrystalline film for self-assembling of Bi particles to form circular clusters each with diameter of ~580nm as shown in figure 1(b). Each cluster consists of Bi agglomerates with broad grain boundaries.

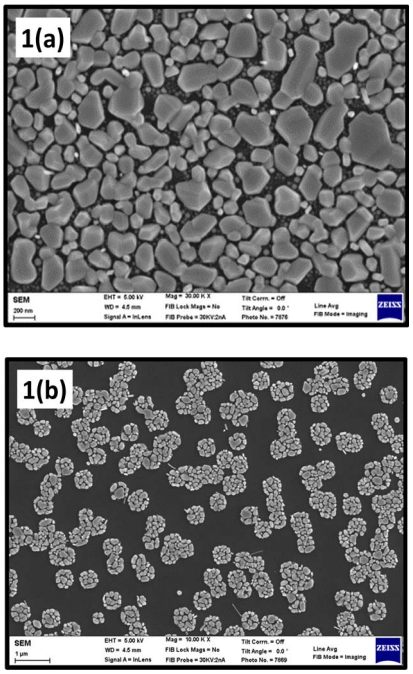

Figure 1. FESEM image of grown Bi nanostructure

Pump-probe measurements were performed using 420nm excitation wavelength to create non-equilibrium electrons in the conduction band and probe the perturbation in energy levels of excited states covering region from visible (450-800nm) to NIR (900-1500nm). Figure 2 shows transient absorption (TA) spectra resulted from UFTS experiment. The obtained TA spectra shows maximum ΔA/A signal at 1ps exhibiting 3 significant features: a broad transient excited state absorption (ESA) in the visible range with a hump at ~600nm followed by a peak at 773nm and broad positive ΔA/A in NIR region with a hump at 1150nm. Being an indirect bandgap semimetal, Bi has indirect overlapping [4] of its valence band with conduction band. This suggests that incident photons (laser pulses) of different energies may cause interband as well as intraband electronic transitions alike metals and semiconductors which is itself a complex study. Thus, the broad transient absorption in visible-NIR region may be attributed to inter- and intra-band electronic transitions.

According to the research reported in literature [5] about Bi films with nanostructured surfaces, its total dielectric function ($\varepsilon = \varepsilon 1 + j\varepsilon 2$) depicts two important features (i) Bi exhibits negative ε1 in UV, visible and near-IR regions while (ii) a strong absorption band in ε2 spectrum centered at 0.8eV (1537nm). The negative ε1 in the UV-visible region is due the plasmonic properties of Bi nanostructures without any contribution of free charge

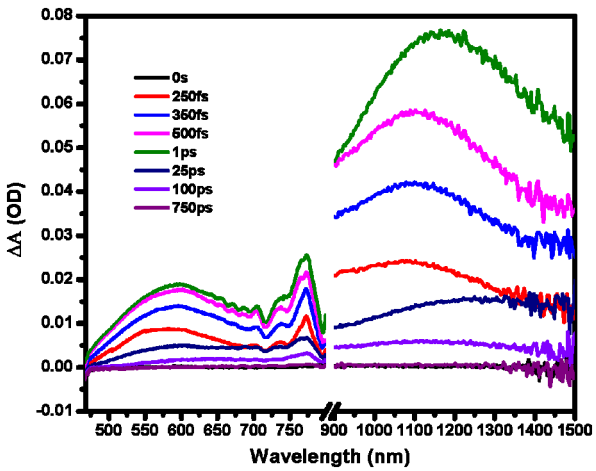

Figure 2. Transient spectra of grown Bi nanostructure excited by wavelength 420nm

carriers rather due to the excitation of interband transitions. On the other hand, these interband transitions are responsible for dominant absorption band in the form of positive ε2. Thus, it is evident that the broad transient ESA is due to collective effect of interband electronic transitions and plasmonic response in this region.

Figure 3 shows the transient decay kinetics of photoexcited charge carriers monitored at 600nm, 773nm and 1150nm. The decay lifetimes has been extracted from the kinetic profile using following equation:

$$S(t) = e^{-\{(t-t_o)/IRF\}2} \sum A_n \, e^{-\{(t-t_o)/\tau_n\}2}$$

It has been found in kinetic profile that ESA at 600nm and 773 nm consist of oscillatory components arising from the coherent phonons [6, 7]. This suggests that ESA in visible region arises due to the contribution of photoexcited carriers, surface plasmons and coherent phonons as well.

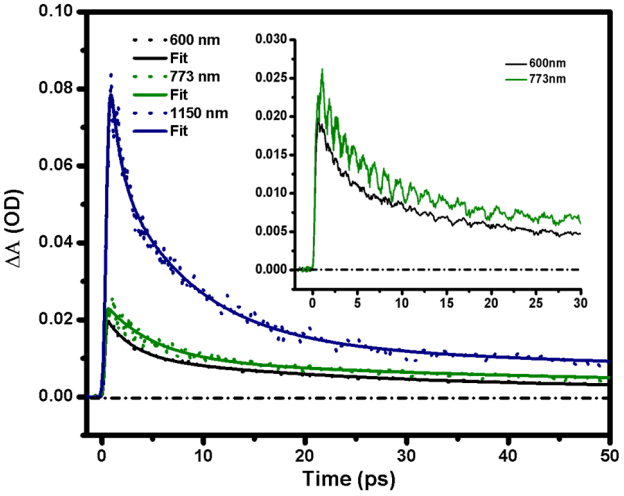

Figure 3. Decay kinetics of the charge carriers absorbed at 600nm, 773nm and 1150nm

This has also been reflected in its decay lifetimes consisting of two majority decay components ($\tau1$ and $\tau2$). The faster decay component ($\tau1$) is due to the surface plasmons while the slower one ($\tau2$) has contribution of phonons. As it can be seen in figure 3 that oscillatory component of decay profile at 600nm is very less and weak as compared to that of profile at 773nm. The decay lifetimes calculated for charge carriers at 773nm ($\tau1$ = 4.91ps and $\tau2$ = 51.6ps) are found to be higher than that of charge carriers at 600nm ($\tau1$ = 2.63ps and $\tau2$ = 23ps). The charge carrier dynamics recorded at 773nm manifest that majority carrier (60.4%) decay in 4.91ps and 29.5% carriers show decay lifetime of 51.9ps while the rest 10.2% of photoexcited carriers took 570ps to recombine. Similarly, the charge carrier dynamics recorded at 600nm manifest that 49.3% carriers decay in 2.63ps and 37% carriers show decay lifetime of 23ps while the rest 13.7% of photoexcited carriers took 200ps to recombine. However, Bi nanostructures have potential to manifest plasmonic effects in the far-IR and THz region arising from excitation of free carriers while the resonances in Bi nanostructures in UV-Vis-near IR region induce by interband transitions, also called as "interband plasmonic" resonances [8]. In addition, Bi shows richness of lower-lying energy bands manifested by its band diagram [9]. These facts suggests that TA spectra manifesting highest signal in near-IR region arises due to higher concentration of lower-lying energy bands in Bi and interband plasmonic resonances in the nanostructure. The decay lifetime calculated at 1150nm exhibit faster decay ($\tau1$ = 0.94ps and $\tau2$ = 7.76ps) as compared to that calculated in visible region. Therefore, the decay kinetics monitored at different wavelengths in visible-NIR region exhibit decay of contributed charge carriers (photoexcited carriers, surface plasmons, phonons) at ultrafast time-scales Hence, this study manifests the dynamic behavior of charge carriers of Bi nanostructure in visible-near IR region upon excited by ultrafast pulses.

4. Conclusion

We have fabricated Bi nanostructure consists of self-assembled nanoclusters. Further tuning of annealing temperature is needed to fabricate fine periodic surface nanostructure, might be nanorods to improve the quality of Bi nanostructure. It will definitely exhibit improvement in its optical properties. This study reports ultrafast charge carrier dynamics of grown Bi nanostructure and the corresponding relaxation of non-equilibrium charge carriers. We have observed positive $\Delta A/A$ signal in visible-NIR region upon photo-excitation of Bi nanostructure by ultrafast pulses. The positive signal is attributed to excited state absorption arises due to various reasons; surface plasmons and phonons in visible region and interband plasmonic resonances in NIR region. The observed features of ultrafast dynamics reflect potential of Bi for applications of solar energy harversting. However, further detailed studies are required to address many theoretical and practical questions, especially to reveal plasmonic properties of Bismuth utilizing ultrafast spectroscopy.

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6. References

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