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Photoluminescence of nanodiamonds influenced by charge transfer from silicon and metal substrates

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ABSTRACT

Photoluminescence of 5 nm detonation nanodiamonds (DNDs) is studied as a function of their surface treatment (hydrogenation/oxidation) and underlying substrate materials (silicon, gold, platinum, and nickel). The substrates affect DND photoluminescence emission spectrum and lifetime in the spectral range of 600–800 nm. The dependence is different for hydrogenated and oxidized DNDs. We attribute these effects to different electrostatic charging of DNDs on the substrates with different work functions (4.4 to 5.5 eV). We discuss the data based on naturally present NV centers, their phonon sideband, and surface-related non-radiative transitions.

1. Introduction

Nanodiamonds (NDs) belong to a family of carbon-based nanomaterials that are promising for numerous applications [1]. The most topical nowadays are applications of NDs in biology [2] such as imaging and drug delivery as well as in spintronics, photonics and quantum information technology [3–5]. The development of these applications gives rise to important progresses in surface modifications of nanodiamonds [6]. Photoluminescence (PL) is the key property in most of these applications. PL of nanodiamonds in visible spectral range can originate from dislocations and point defects [7], various color centers such as nitrogen or silicon vacancy centers (NV, SiV), and surface-related transitions in sp^2 carbon phase (often forming ND shell), surface defects, and surface chemical moieties [8–11].

Photoluminescence of NDs is indeed to a great extent determined by the structure and chemistry of the surface due to considerable surface to volume ratio. For instance, ND surface termination was shown to control photoluminescence of NV centers. In particular, hydrogenation of NDs leads to quenching of luminescence related to negatively charged (NV^-) centers and as a result produced color shifts from NV^- (638 nm) to neutral NV^0 (575 nm) photoluminescence [12]. Similarly, high quality surface oxidation [13] or fluorination (on both bulk diamond [14] and nanodiamonds on Pt substrate [15]) lead to enhancement of NV^- over NV^0 color center population compared to hydrogen-terminated diamonds.

Here we report another, novel effect that arises from the substrate the NDs reside on. Effect of substrate on electronic and PL properties of nanostructures such as graphene oxide [16] or MoS_2 [17] has been recently demonstrated. Similarly, we have demonstrated that NDs inherently accommodate their electrical potential to the substrate, resulting in up to 0.4 V different potential of the same nanoparticles on Au and Si substrates [18]. This effect was attributed to charge transfer and trapping on the nanoparticles which was dependent on the substrate material as well as on the surface termination of NDs. The effect was also independently confirmed by observation of different emission of secondary electrons in a scanning electron microscope (SEM). Here we show that the inherent charge transfer between NDs and substrate influences also photoluminescence of NDs in terms of PL spectral shifts and lifetimes. We also show that the PL changes depend on whether NDs are hydrogen or oxygen terminated and we discuss the data based on naturally present NV centers and their phonon sideband.

2. Experimental

As diamond nanoparticles we used detonation nanodiamonds (DNDs) provided by the NanoCarbon Research Institute Co., Ltd.

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(Japan) with nominal size of 5 nm. We compare hydrogenated (H-DNDs) and oxidized (O-DNDs) prepared by micro-wave enhanced plasma hydrogenation [19] or oxidation by air annealing [20]. The DNDs were dispersed in water by ultrasonication. The DNDs were de-agglomerated when dispersed in solution. The DLS, TEM and other basic characteristics of the employed DNDs are provided in our prior publication [18]. The colloidal dispersions were appropriately diluted in order to deposit only a thin layer of DNDs on the substrates by drop casting.

The substrates were n-type Si wafers (10 Ω cm) with various metals deposited (by sputtering or thermal evaporation) in the thickness of about 50 nm on top: Au, Pt, and Ni. The substrates provide a large range of surface work functions: Si 4.35 eV, Au 5.0 eV, Pt 5.2 eV, Ni 5.45 eV. We always combined two materials (from Si, Au, Pt, Ni) on one substrate for mutual reference.

For PL imaging we used an Olympus IX71 inverted optical microscope with 100 W mercury lamp (U-LH100HG) as the light source, WIGA fluorescence filter cube, and UPlanFL 20× objective [10]. The filter cube consisted of green excitation band pass filter (530–550 nm), red emission band pass filter (575–625 nm), and corresponding dichroic mirror. The exposure time was 20 s.

For measurements of PL spectra and time-resolved PL we used a custom built confocal fluorescence microscope using 514 nm green laser (~2 mW) for excitation through objective (100×, 0.7 NA) with confocal spot of about ~500 nm. Emitted PL was collected through a dichroic mirror, long pass filter and directed to an avalanche photo diode (APD) or a spectrometer [21].

3. Results

Fig. 1 shows optical and fluorescence images of H-DNDs measured at Au/Si and Ni/Pt boundary. Optical images in Fig. 1a and c show that the surface is coated mostly by a thin DND layer (thickness 20–50 nm estimated by atomic force microscopy). Dark dots correspond to large DND clusters arising from the deposition process. Thus the fluorescence originates mostly from DND clusters and not from single particles. Yet note that as the DNDs were de-agglomerated in the solution the DND clusters on the surface are composed of truly single particles bound by Van der Waals forces. This is thus different to the typical DND agglomerates in detonation soot (referred to as core agglutinates). To obtain background reference from the substrate the DND layer was partially removed from the substrate mechanically along a horizontal direction. This region is visible as brighter stripe in the optical images in Fig. 1a and c.

Corresponding fluorescence images in Fig. 1b and d show that there is a large difference in PL intensity of H-DNDs on the Au and Si substrate: H-DNDs on Si exhibit 2% of the PL intensity they exhibit on Au (intensity averaged in the area of 30 × 30 μm^2). On the other hand, there is no noticeable difference between PL on Ni and Pt substrates. Thus it is not the difference in substrate work function and corresponding different charge of the nanoparticles that control the overall PL intensity. The most likely reason is difference in the substrate reflectivity. As can be seen in optical images, Ni and Pt exhibit similar reflectivity while Au reflects more light than Si. This is well correlated with the observed PL intensity. At the same settings, O-DNDs showed much weaker PL intensity, difficult to detect vs. background (images not shown).

On the other hand, PL spectra in Fig. 2 show broad PL band around 700 nm that shifts in dependence on the substrate material. Note that the spectra in Fig. 2 were normalized due to different PL intensities on different substrates and on differently terminated nanodiamonds. For O-DNDs (Fig. 2a) the PL maximum remains about the same for Si and Au at 680 nm while for Ni it shifts to about 700 nm. The trend is different for H-DNDs. Fig. 2b shows that PL maximum is about the same at 660 nm for Si and Ni while it shifts to 640 nm for the Au substrate. In both cases the difference is about 20 nm. The PL shift thus depends on the work function of the substrate with a non-uniform trend. We measured time-resolved PL to obtain more insight into the kinetics of photogenerated charges in DNDs on various substrates.

Fig. 3 shows examples of PL decay profiles of H-DNDs and O-DNDs on Au and Ni. The presented PL decay profiles are typical and they are well reproducible across the sample. The decays were measured as integrated PL intensity after the excitation by picosecond laser at 514 nm. PL decays were measured on all the substrates; we only selected the two

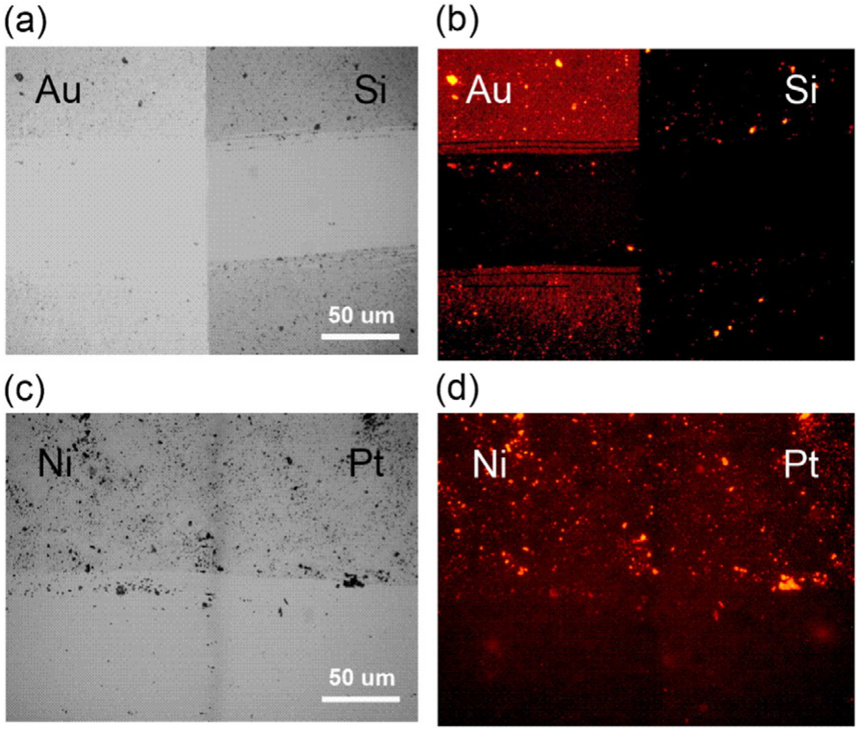

Fig. 1. Optical (a, c) and fluorescence microscope images (b, d) of H-terminated DNDs measured at Au/Si and Ni/Pt boundary. The DND layer is partially removed from the substrate mechanically along horizontal direction to provide the background reference.