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Manipulations with Diamond Nanoparticles in SPM: the Effect of Electric Field of the Conductive Probe Tip

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Abstract—The role of the electric field during manipulations with diamond nanoparticles on a silicon substrate by a scanning probe microscope (SPM) tip is studied. It is found that the attractive force appearing in the contact between nanodiamond and an electrically charged tip is sufficient to detach and displace a chosen nanoparticle from initial to goal position under moderate mechanical stresses of the probe to nanoparticle. The problem of the control of the tip motion trajectory during manipulations is solved by visualizing the tip trace of the sample surface. The results obtained will be used for precision positioning of single-photon emitters based on luminescent nanodiamonds in microcavities.

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The diamond containing color centers is one of the most attractive objects for producing single-photon emitters (SPEs), since even single color centers, e.g., "nitrogen-vacancy" or "silicon-vacancy" exhibit high-stability and -intensity photoluminescence at room temperature [1–4]. There are two main directions in the formation of a tailored SPE architecture in diamonds: (i) one emitter or an array of emitters is formed in the diamond bulk crystal, (ii) one emitter is formed in an individual diamond nanocrystal. A disadvantage of the first approach is the complicated SPE fabrication in a certain position if, e.g., the SPE is formed by diamond doping with impurity atoms during its synthesis, and the impossibility of modifying a once fabricated structure. The second approach seems more promising, since it allows free operation with such emitters, i.e., their proper orientation in space and formation of arrays of single-photon emitters of any required configuration.

Two main stages can be distinguished in the formation of ordered nanodiamond structures: (i) the "probabilistic" and then (ii) "deterministic" distribution of luminescent nanoparticles over the substrate [5, 6]. During the "probabilistic" distribution, e.g., using centrifuging or drop techniques, nanodiamonds are randomly applied on the active substrate area. Then, diamond nanoparticles are post-selected and structures are post-processed using nanomanipulations. For the "deterministic" distributions of nanoparticles, the "pick and place" method is mostly used, according to which nanoparticles preliminarily selected using, e.g., a confocal microscope, are separated from the substrate, are transferred to a chosen structure, and then are fixed in a new position [7–9]. As a nanomanipulation tool, the scanning probe microscope (SPM) tip is used in most cases. An important advantage of the "pick and place" technique is the process scalability. The second, third, and other nanoparticles are positioned only when the first particle occupied the position. The number of successful manipulations in this method is $\sim 1/3$ of the total number of attempts, since nanodiamond often does not adhere to the tip or adheres to its end face and becomes unidentified during the initial and subsequent scans [6].

As a nanomanipulation technique version, the method hereafter referred to as "pushing" can be noted. The manipulation tool, i.e., the SPM tip, is forced to the substrate surface and is placed into continuous contact with the nanoparticle, functioning as a mechanical pusher for the nanoparticle over the sample

surface from one position to another [10]. The active filed is cleaned from excess nanoparticles in the same way.

The implementation of successful manipulations depends to a large extent on the nature and degree of the interaction of the diamond nanoparticle with the SPM tip. In the "pick and place" method, the nanodiamond is separated from the substrate due to an extremely strong mechanical stress of the tip to nanoparticle, close to the ultimate strength (the tip is forced to the nanodiamond with a force to 1 μN), which is necessary to achieve nanodiamond adhesion to the tip, sufficient to overcome the Van-der-Waals attractive force of the nanodiamond to the substrate [6]. In comparison with the "pick and place" technique, the nanodiamond displacement and motion to a new position in the "pushing" technique do not require such significant forces. However, the relatively weak tip–nanoparticle interaction (even taking into account the capillary forces acting in the nanoparticle–tip region in the presence of a water adsorbate) has also negative aspects: the force should be applied to a certain tip contact point strictly toward the nanoparticle center of mass, which is a difficult problem in view of the topological variety of diamond nanoparticles, and the nanoparticle should be moved along a straight line; otherwise, the nanoparticle can be spontaneously detached from the tip [11].

Thus, it is an important problem to include an additional channel of the SPM tip–nanodiamond interaction to the nanomanipulation process, which would make it possible, on the one hand, to weaken mechanical stresses in the tip–nanodiamond contact; on the other hand, to increase the nanodiamond adhesion to the tip. In this work, the new channel of the tip–nanodiamond interaction, i.e., SPM tip electric field induced due to applying an electrical voltage between the conductive tip and sample is studied.

Diamond nanoparticles with an average size of ~100 nm (Tomei Diamond Co., Japan) were deposited on a silicon substrate 1×1 cm^2 in area from an aqueous solution. To improve hydrophilic properties, the substrate was annealed at a temperature of 700 °C for 5 min. A colloidal solution of nanodiamonds (with a concentration of 1 g/l) was prepared by mixing a dry diamond powder in distilled water using an ultrasonic bath. Seeding was performed by centrifuging of a solution drop on the silicon surface.

Experiments with nanodiamond manipulation were performed using a Solver P47 SPM in air at relative air humidity $RH = 30$–50%. A silicon cantilever with a tip coated with a Pt–Ir layer was used as a conductive probe. The typical force constant is 0.6 N/m, the tip end radius is ~30 nm.

The nanodiamond manipulability by the "pick and place" and "pushing" methods was tested in the experiments. Before and immediately after manipulations, the surface relief was inspected by scanning in the tapping mode.

In the "pick and place" method, we used the following manipulation order: (a) the tip (it is positioned at the scan field center after the scanning end) is guided to a chosen nanoparticle taking into account the correction for displacement, an electrical voltage of +10 V is applied between the sample and tip, and the tip is placed into contact with the surface for ~1 s ("pick" stage); (b) the tip is moved to a new point and is placed into contact with the surface for ~1 s at a voltage of −10 V ("place" stage).

Manipulations by the "pushing" method were performed at a constant tip pressure to the surface (contact mode). The particle translatability was tested by scanning the probe (tip) along a target trajectory with simultaneous applying single positive voltage pulses 100 ms long at each point (pixel) with amplitude $U_i = +10$ V to the sample (the probe is grounded). We note that a standard setpoint was set in all contact mode experiments, which provided a moderate tip pressure on the sample.

Simultaneously, one more problem, i.e., the tip path control, was solved. The way of solving the problem is visualization of the tip "trace" on the surface sample in the SPM when the tip contacts with the substrate. As a main method for forming the trace, local oxidation of the substrate material (silicon in the case at hand) in the presence of a water adsorbate on the sample surface is considered. According to the trace position with respect to the nanoparticle, corresponding corrections to the tip trajectory on the sample surface were introduced.

The use of the electrically biased tip in nanodiamond manipulations made it possible to displace nanoparticles from one position to another by the "pick and place" method without strong mechanical loads on the tip. Figure 1 shows the displacement of a nanodiamond ~100 nm in size from position (A) to position (B) by the "pick and place" method at a tip load of ~0.1 μN.

It was found that successful manipulations with nanoparticles can be performed only using corrections for the actual pressed tip end position with respect to the nanoparticle. The point is that the surface

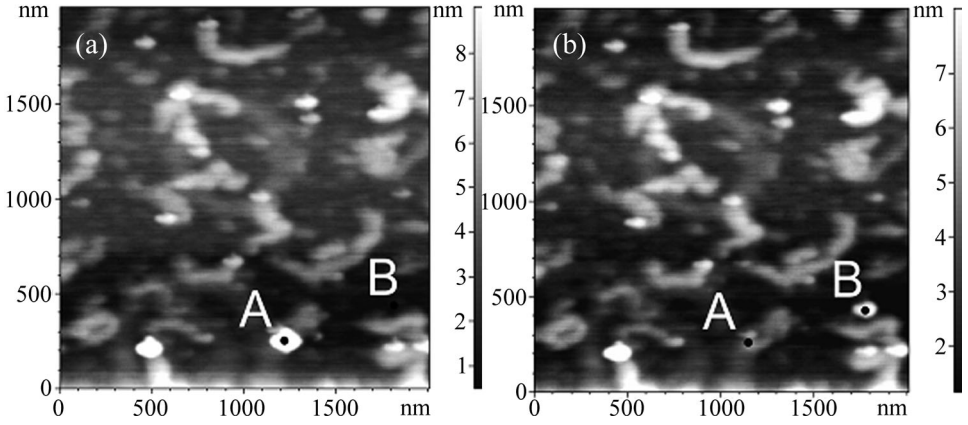

Fig. 1. Result of nanodiamond displacement (transfer) from point A to point B by the "pick and place" method.

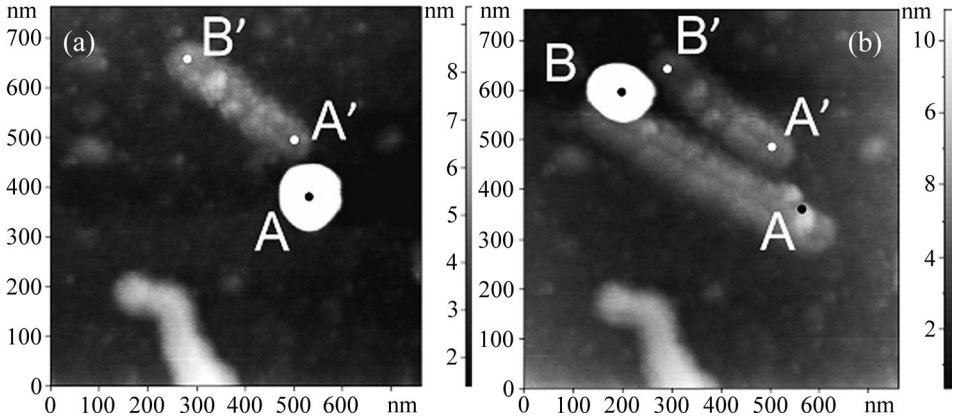

Fig. 2. Manipulations with a diamond nanoparticle in the contact mode when applying an electric field between the sample and electrical voltage probe: (a) after the first attempt of nanoparticle displacement; (b) relief map after the second attempt of nanoparticle displacement. The trace of electric influences shows the actual trajectory of SPM tip end displacements.

relief map used for "aiming" the tip to the nanoparticle is recorded in the tapping mode. This map has a significant spatial shift with respect to the map recorded in the contact mode. This shift is explained by the difference in the SPM probe pressure to the surface and, hence, tip bending in various scanning modes. Therefore, at identical scanning setting parameters, but in different modes, the tip contacts with the sample surface (probes the sample) at different points.

Based on the data on the coordinates of the trace of the electrically biased tip on the (silicon) substrate surface, corrections for the tip position were introduced. It was found that in the case of a positive voltage applied to the sample, the trace manifests itself as an extensive ridge on the sample surface. This result confirms that the case in point is the silicon anodic oxidation reaction at the contact with the SPM tip in the presence of a water adsorbate [12]. The trace visualization in the SPM makes it possible to reveal whether the tip trajectory crossed the position of a given nanoparticle. Manipulations in this situation are illustrated in Fig. 2. As a result of scanning of a surface area of 750×750 nm^2 in the tapping mode, nanoparticle (A) was detected, which appears in the SPM map as a bump $\sim$150 nm in diameter (see Fig. 2(a)). Then it was attempted to displace this nanoparticle. To this end, the SPM was switched to the contact mode, the tip was aimed to the nanodiamond position point in the relief map (point A), and the tip was displaced along a set trajectory with simultaneous applying electric pulses. After repeated recording of the relief in the tapping mode and visualizing the tip displacement trace, it was found that the starting point is in fact shifted upward and to the left with respect to the nanoparticle position (point A' in Fig. 2(b)) and the trajectory passed by the nanoparticle (path A'B' in Fig. 2(a)). The data obtained

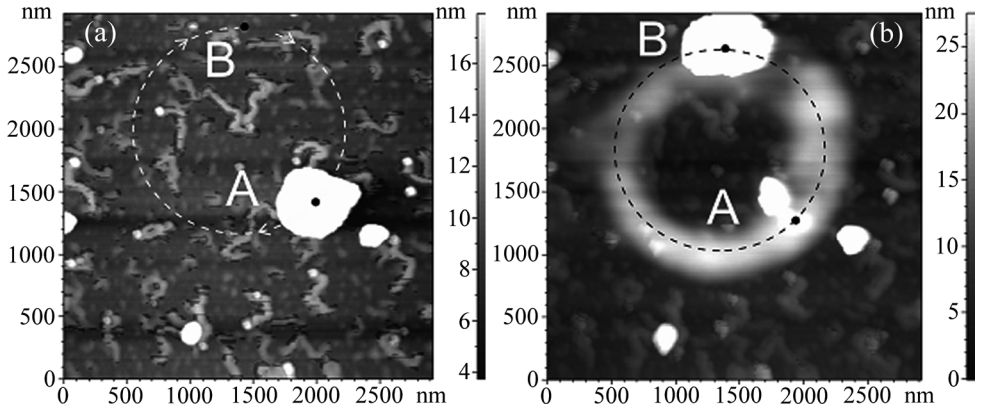

Fig. 3. Manipulations with a nanodiamond cluster: (a) starting position of nanoparticle (A), (b) nanoparticle position after a complete revolution of the probe from point B over a complete clockwise circle. The probe path is shown by the dashed curve. A ring-shaped bump appeared along the probe path.

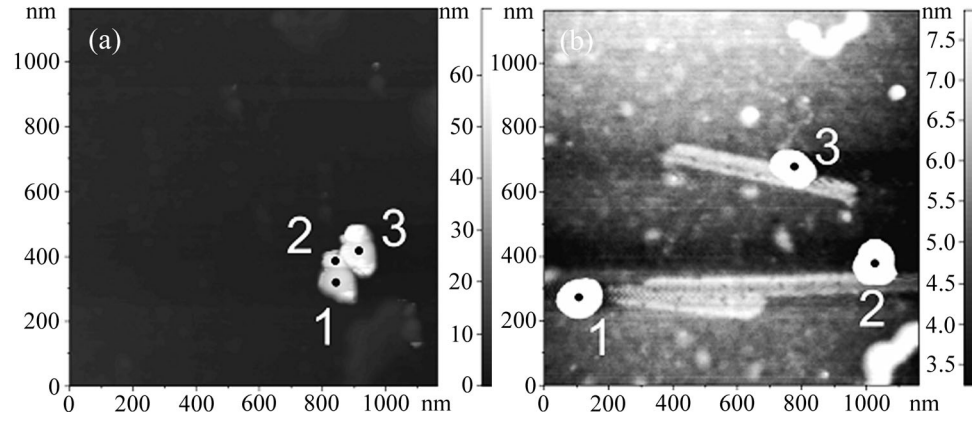

Fig. 4. Manipulations with a nanodiamond cluster: (a) starting position, (b) partition into individual nanoparticles.

were used to properly correct the tip trajectory with the result that it became possible to displace the nanoparticle from point A to point B (Fig. 2(b)).

The electrically biased tip allowed displacements of not only individual nanoparticles over the substrate surface but also clusters and along nonlinear trajectories (Fig. 3), which is almost impossible in the case of a purely mechanical displacement of the nanodiamond by the tip. Figure 3 shows the displacement of a cluster with a lateral size of ~500 nm (nanoobject A on Fig. 3(a)). The tip was clockwise moved in the contact mode from point B through point A over a full circle. As seen in Fig. 3(b), during the probe tracing, most cluster nanoparticles transferred from point A to point B, i.e., made ~2/3 of full circle, and several nanoparticles remained in the initial position. The probe path was imaged in the relief map as a ring-shaped bump (see Fig. 3(b)).

Another operation which can be performed using the electrically biased SPM tip is nanodiamond cluster discretization into individual nanoparticles. Figure 4 shows the discretization of the nanodiamond cluster including $\geq$3 nanoparticles (see Fig. 4(a)) into individual nanoparticles. Using the electrically biased tip, nanodiamonds were separated and displaced to new positions in the scan field: nanoparticle 1 – to a distance of ~1 μm to the left, nanoparticle 2 – to the right, and nanoparticle 3 – over a complex trajectory upward to the left (Fig. 4(b)).

A convincing example of the efficiency of the attractive force created by the charged probe was obtained in an additional series of experiments with a conductive nanocrystalline diamond film grown by the PCVD method in a N_2:H_2:CH_4 gas mixture on the silicon substrate [13]. The film thickness is ~150 nm. Nanodiamond cohesion in the nanocrystalline film is *a priori* higher than that of seeded nanodiamonds with the silicon substrate; however, it manages to trap a nanoparticle and to displace it to a new position even in this case.

We associate the mechanism of the observed effect of nanodiamond attraction to the SPM tip with the electrostatic force created by the probe charged by electrons. We note that a similar mechanism takes place when the SPM tip is irradiated with an electron beam under vacuum conditions [14]. The new method for manipulating diamond particles in the SPM, i.e., trapping of nanoparticles and their displacement over the sample surface by the electrically biased SPM tip showed its efficiency and imparted a new quality to the manipulation process based on both the "pick and place" and "pushing" techniques. In particular, in comparison with mechanical manipulations, the "pick and place" technique using an electrically charged tip makes it possible to decrease the level of mechanical stresses at the tip–nanoparticle contact and to increase nanoparticle adhesion to the tip in the "pushing" technique. During the experiments, an approach was found to solving one more important problem of nanoparticle manipulation, i.e., *in situ* control of the tip trajectory over the sample surface. The basic principle of this operation is the observation of the trace from the effect of the electrically charged SPM tip on the substrate surface. Under conditions of humid medium and in the presence of a water adsorbate on the substrate surface, the formation of such traces is caused by the local electrochemical oxidation reaction of a material (silicon in the case at hand).

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