Surface coating with oxide layers to enhance the spin properties of shallow NV centers in diamond

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We present an enhancement of spin properties of the shallow (<5nm) NV centers by using an ALD to deposit titanium oxide layer on the diamond surface. With the oxide layer of an appropriate thickness, increases about 2~3.5 times of both evolution time ($T_2^\ast$) and relaxation time ($T_1$) were achieved and the shallow NV center charge states stabilized as well. Moreover, the coherence time ($T_2^*$) kept almost unchanged. This surface coating technique could produce a protective coating layer of controllable thickness without any damages to the solid quantum system surface, making it possible to prolong $T_2^\ast$ time and $T_1$ time, which might be an approach to the further packaging technique for the applying solid quantum devices.

The nitrogen-vacancy (NV) center in diamond has been considered to be prospective in both quantum information science and precision measurement owing to its outstanding spin properties at room temperature. For example, quantum registers based on the coupling of two NV centers have been experimentally demonstrated. Measuring techniques of electric and magnetic fields, temperature etc., by using NV centers in diamond have driven to maturity stage. It is of interest to make the solid quantum system of diamond NV center a device for application. However, in experimental quantum information science, one challenge is to insulate the quantum systems from the external interferences. Up to now, a number of experimental schemes to relieve the influences from diamond surface or outer environment have been presented and tested by many groups. One familiar and effective method is to make the diamond surface O-terminated or N-terminated etc., called surface termination. However, this surface treatment can provide only an atom-thick layer on the diamond surface and the limited layer thickness may not meet the needs of packaging technique. Moreover, thermal oxidation or plasma etching used to obtain the satisfactory surface termination damages the diamond surface irreversibly, etching away the very shallow (<5nm) NV centers. Hence a method which can produce a protective layer of controllable thickness without any surface damages to prevent from etching shallow centers away is being sought.

In this letter, we demonstrate an enhancement of the spin properties of shallow NV centers by depositing titanium oxide coating layer on the diamond surface without any surface damages. We performed atomic layer deposition (ALD) to deposit nanoscale titanium oxide which is nonmagnetic and non-fluorescent at room temperature as surface coating layer. Before and after ALD, we studied the variations of shallow center spin properties, such as free induced evolution time ($T_2^\ast$), coherence time ($T_2$) and spin-lattice relaxation time ($T_1$), the behaviors being frequently-used in various applications. We also studied the relevance between spin properties and layer thickness. This surface coating technique may contribute to the prospective packaging technique for devices made of diamond NV center systems.

An array comprising 60 nm diameter apertures was patterned on a 300-nm-thick polymethyl methacrylate (PMMA) layer deposited beforehand on the surface of an electronic grade diamond substrate from Element Six. By ion implantation with the $^{14}N_2^+$ molecule energy of 50 keV and a fluence of $6.5 \times 10^{11}$ $^{14}N_2^+$ per cm$^2$ through the apertures, the NV center array was created with a probable depth of about 33 nm (obtained by SRIM). Afterwards, the implanted diamond substrate was annealed at 1050 °C in vacuum at $2 \times 10^{-5}$ Pa for 2 h, and then boiled in a 1:1:1 mixture of sulfuric, nitric, and perchloric acids. The fluorescence image of a representative area of NV center array after all the processes above implemented is shown in Fig.1(a) where the lightspots represent NV centers and the fluorescence intensity of a single NV (verified by its $g(2)(0)$ value much less than 0.5) is about 30 k/s.

To obtain shallow centers, we performed plasma etching by using a reactive-ion-etch (RIE) reactor (Oxford PlasmaPro NGP80 machine). The diamond plate was etched in conditions of 200 w ICP power, 30 mTorr chamber pressure, 10 sccm of oxygen, 5 sccm of argon, with an etching rate of 11.4 ± 2 nm/min. We applied a 150-second plasma etching on the diamond (corresponding to an etching depth of about 28.5 nm) to make most NVs locate at the depths less than 5 nm from the surface. Using the shallow centers obtained by plasma etching rather than using the ready-made shallow centers generated by low energy implantation was because we could contrast the etched shallow center behaviours after ALD with the ones of these centers locating deep in the diamond before etching to verify the effects of surface coating. On the other hand, the first cycle of $H_2O$ in the de-

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position processes would make the diamond surface O-terminated, so we made the sample surface O-terminated by oxygen plasma etching before surface coating to eliminate the contribution of oxygen termination to the spin property variations in contrastive study.

The diamond sample was then put into the ALD chamber (Picosun, Sunale R-200 Advanced) to deposit titanium oxide layer (Ti,O$_x$ layer, abbreviated as TOL hereafter). The first atomic deposition cycle of H$_2$O cycle would make the hydroxyl ions absorb on the sample surface. Then the titanium ions from the second deposition Ti cycle would replace the hydrogen ions of hydroxy. We repeated the above two cycles sequentially to deposit the oxide layer on the diamond surface. (An additional H$_2$O cycle was always applied in the end of all ALD processes.) The deposition rate of TOL was about 1 nm for every nine-ALD cycle at the temperature of 120 °C. Before and after ALD, the sample surface was characterized with X-ray photoelectron spectroscopy (XPS) to verify if the TOL had been deposited on the surface.

Figure 1(b) exhibits the high-resolution XPS carbon 1s spectrum of the sample surface after ALD, showing a dominant diamond sp$^3$ peak at 286.5 eV, accompanied with three side peaks, from left to right, assigned to carbon doubly and singly-bonded to oxygen, and sp$^2$ carbon. Comparing Fig. 1(b) with the XPS result of carbon 1s spectrum of the same sample before ALD (not shown in this letter), the two spectra were almost identical. Figure 1(c) presents the high-resolution XPS titanium 2p spectra. The dotted line shows the result before ALD from which no titanium related peaks are obtained, while the solid line represents the result after ALD from which distinct peaks belonging to Ti 2p spectrum were found around 459 eV. Another proof to certify the success of depositing oxide layer on the diamond surface was the XPS survey scan exhibited in Fig.1(d), showing the relative intensity of oxygen and carbon peaks. The intensity of oxygen peak raised remarkably relative to the intensity of carbon peak, revealing that after ALD, the main component of characterized sample surface changed from carbon to oxygen, i.e., the oxide layer had been indeed deposited on the surface. Moreover, the appearance of Ti peaks in Fig.1(d, bottom) demonstrated that the protective layer was made up of titanium oxide.

The diamond sample was placed in the custom-built confocal microscope system with the applied magnetic field (B = 55 ± 5 G) parallel to the detected sin-
Figure 3. $T_2^*$, $T_2$ and $T_1$ measurements of the labeled shallow single NV centers before and after ALD. (a) The Ramsey measurements of NV-03 before ALD (top-left), after depositing 4 nm TOL (bottom-left), after depositing 8 nm TOL (top-right), and initially at the depth about 33 nm (bottom-right), respectively. (b) The Ramsey measurements of five typical centers before ALD, after depositing 4 nm TOL and after depositing 8 nm TOL. (c) The spin echo measurements of NV-16 before ALD (top-left), after depositing 4 nm TOL (bottom-left), after depositing 8 nm TOL (top-right), and initially at the depth about 33 nm (bottom-right), respectively. (d) The spin echo measurements of five typical single centers before ALD, after depositing 4 nm TOL and after depositing 8 nm TOL. (e) $T_1$ measurements of NV-01 before ALD, after depositing 4 nm TOL and after depositing 8 nm TOL. (f) $T_1$ measurements of four typical single NV centers before ALD, after depositing 4 nm TOL and after depositing 8 nm TOL.

Single center axes. The ALD was performed twice in succession to study the influence of TOL thickness on spin properties. Twenty shallow single NV centers (labeled NV-01~20) were measured before and after each ALD. Figure 2(a) demonstrates the fluorescence images of the same single center (NV-02) after each step. This representative center initially sat at the depth of about 33 nm with its photoluminescence (PL) intensity of about 28k/s [Fig.2(a) bottom-right]. After proper etching treatment NV-02 became close to the surface with its depth less than 5 nm and its PL intensity decreased to less than 10k/s [Fig.2(a) top-left] owing to the unstable charge state of shallow center. When a 4-nm-thick TOL was deposited on the diamond surface, the PL intensity of NV-02 increased to about 15k/s [Fig.2(a) bottom-left], indicating that its charge state became stable. Moreover, after another 4-nm-thick TOL being deposited (8 nm in total), the NV-02's PL intensity increased to about 28k/s [Fig.2(a) top-right], similar to its initial PL intensity. For all the measured single centers, their PL intensities changed in the same way. As stated above, the TOL in our experiment was nanoscale so that the optical collection efficiency of objective was unchanged. Therefore, the increase of NV center’s PL intensity demonstrated that the charge states of shallow NVs could stabilize by surface coating titanium oxide protective layer.

The variations of free induced evolution ($T_2^*$), coherence ($T_2$) and spin-lattice relaxation ($T_1$) arising from the deposited TOL were studied by applying basic microwave (MW) pulse sequences [Fig.2(b)]. The oscillating curves of evolution times were fitted with the function

$$I(t) = I_0 + A_0 \exp\left[-(t/T_2^*)^n\right] \sum_{i=1}^{3} \cos(2\pi\delta_id + \phi_i)$$

to deduce the spin dephasing time $T_2^*$, where $\delta_i$ is the detuning frequency and the exponential index $n$ is set to be 2 corresponding to the Gaussian dephasing case. To acquire the values of $T_2$ times, we fitted the data by a stretched exponential envelope multiplied by a periodic Gaussian function

$$C(t) = C_0 + A_0 \exp\left[-\left(\frac{t}{T_2}ight)^n\right] \sum_{i=1}^{3} \exp\left[-\left(\frac{t - i \times T_R}{T_C}\right)^2\right]$$

where $T_2$ is the decay time of the envelope of revival peaks, $T_C$ is the decay time of initial collapse, and $T_R$ is the revival period time of revival peaks. The $T_1$ times
For the longitudinal spin relaxation time \( T_1 \), a representative result of the center NV-01 is demonstrated in Fig.3(e). After etching the sample surface but with no TOL on it, this shallow center’s \( T_{1,0nm} \) time was deduced to be about \( 0.107 \pm 0.008 \) ms. After the 4-nm-thick TOL was deposited, the value of \( T_{1,4nm} \) increased to \( 0.524 \pm 0.026 \) ms by a factor of about 5. However, when the TOL was thickened to 8 nm, the \( T_{1,8nm} \) of NV-01 dropped to \( 0.325 \pm 0.014 \) ms. The variations of all 20 measured centers’ \( T_1 \) times conformed to the rule: \( T_{1,4nm} \approx 4 \sim 5T_{1,0nm}, T_{1,8nm} \approx 2 \sim 3.5T_{1,0nm} \), that is \( T_{1,0nm} < T_{1,8nm} < T_{1,4nm} \) as demonstrated in Fig.4(f) for four typical centers.

A number of prior works have investigated the various factors affecting the spin properties. It is acknowledged that \( T_1 \) measured by spin echo is governed by low-frequency (\( \sim \)kHz) noises and \( T_2^* \) can be influenced by the noises of even lower frequency (\( < \)kHz), while \( T_1 \) is sensitive to high-frequency noises.\(^9\)\(^{30,31}\) For the first ALD, that the TOL could be deposited on the diamond surface indicated that the O-terminated surface obtained by oxygen plasma etching was incomplete, leaving a few unpaired electrons (dangling bonds), hydrogen and magnetic ions on the surface. These electrons and ions were connected to or displaced by titanium or oxygen atoms during ALD. The elimination of surface spin baths led to the reduction of very low frequency (\( < \)kHz) noises, so \( T_2^* \) times increased slightly. However, the low-frequency (\( < \)kHz) noises were not related much to the surface,\(^9\)\(^{31}\) so the first ALD did not influence \( T_2 \) time. The depth dependent decoherence was considered to be connected with the magnetic and electric fields produced by surface spins previously,\(^6\)\(^,\)\(^{21,24,30}\) nevertheless, the main source of external fields should be more, in our assumption, attributed to the polar bonds like C-O bonds on the diamond surface since the interfacial fields were nearly unchanged before and after the first ALD as indicated by the almost unchanged \( T_2 \) times. As for the increase in \( T_1 \) time, the decrease of magnetic ions absorbing on the diamond surface and the reduction of surface effects would be responsible.\(^9\)\(^,\)\(^{25,31}\)

As the TOL was thickened from 4 to 8 nm, \( T_1 \) reduced while \( T_2^* \) sharply increased. To understand this, we compared the two ODMR spectra of the same center with 4 and 8 nm TOL on the surface without any applied magnetic fields. Although both ODMR spectra were obtained in the same measurement condition of -10 dBm MW power, an inappreciable dip around 2.87 GHz was found in the spectrum in the case of 8-nm-thick TOL [triangle symbols] shown in Fig.(4). To eliminate the line broadening existent under strong applied fields, we lowered the MW power to -20 dBm and the dip [rhombus symbols] became distinct. Lowering again the MW power to -30 dBm, the ODMR spectrum [circular symbols] showed a split around 2.87 GHz. The curves were obtained by using Lorentz fit and six peaks could be acquired. Except for the interval between peak-3 and peak-4, all the other intervals between two adjacent peaks

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**Figure 4.** Zero field CW-ODMR spectra of the same single NV center with microwave power -10 dBm after depositing 4 nm TOL and -10 dBm, -20 dBm, -30 dBm after depositing 8 nm TOL, from top down in order respectively, the solid curves is the Lorentzian fitting to the experimental spectra.
were about 2.2 MHz, coinciding with the hyperfine coupling constant of $^{14}\text{N}$. It was well-known that the hyperfine splitting of $^{14}\text{N}$ would produce three peaks and that here it ulteriorly divided into two groups of six peaks was owing to the existense of additional electric or strain field. This additional field was introduced from the external stress generated by lattice mismatch of the unbroken expanse of TOL with the intensity of about 6 MHz as derived from the fitting curve, leading to the reduction of both $T_1$ and $T_2$ times. Although $T_1,_{8.0nm}$ decreased after the second ALD, it was still longer than $T_1,_{0.0nm}$ of the very shallow NVs without surface coating, i.e., the spin property was generally enhanced. Moreover, it has been reported that $T_2$ is enormously influenced by inhomogeneous magnetic fields while the external stress can suppress this influence to prolong the $T_2$.

Therefore, the different behaviors of spin properties were due to the appearance of external stress. In addition, we found a few centers' $T_2^*_{8.0nm}$ were even larger than their $T_2^*_{50keV}$ like NV-03 shown in Fig.3(a), suggesting that a part of the inhomogeneous magnetic fields were attributed to the applied magnetic field by using alternating electromagnet.

Consequently, using ALD technique to deposit titanium oxide layer can enhance the spin properties of shallow NV centers in diamond with an increase about 2~3.5 times for both relaxation time ($T_1$) and evolution time ($T_2$) with almost unchanged coherence time ($T_2$). This surface coating produces a protective layer of controllable thickness on the surface of solid quantum system like diamond NV center without any surface damages. Furthermore, this technique may also provide a possible approach for packaging technique for diamond NV center devices used in quantum information science and precision measurement.

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