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Fabrication of a nanometric Zn dot by nonresonant near-field optical chemical-vapor deposition

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We demonstrate a technique for the deposition of nanometric Zn dots by photodissociation of gas-phase diethylzinc using an optical near field under nonresonant conditions. The observed deposited Zn dot was less than 50 nm in size. The photodissociation mechanisms are based on the unique properties of optical near fields, i.e., enhanced two-photon absorption, induced near-field transition, and a direct excitation of the vibration-dissociation mode of diethylzinc. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1394955]

Optical near fields have been applied to high-resolution optical microscopy, high-density optical memory, atom manipulation, and so on.[1] Their application to nanostructure fabrication has the potential to make high-density nanometric-integrated photonic devices possible.[2] Recently, we demonstrated the feasibility of chemical-vapor deposition (CVD) of Zn dots using optical near-field techniques.[3–5] In our previous research, we utilized the high spatial resolution capability of the optical near field to deposit Zn wires with a width of 20 nm (Refs. 3 and 4) and Zn dots 60 nm in size.[5] The size of the objects deposited by conventional far-field optical CVD techniques was found to be diffraction limited. Conventional optical CVD utilizes a two-step process: photodissociation and adsorption. For photodissociation, the far-field light must resonate the reacting molecular gasses in order to excite molecules from the ground to the excited electronic state.[6,7] The Frank–Condon principle claims that this resonance is essential for excitation.[6] The excited molecules then relax to the dissociation channel, and the dissociated Zn atoms adsorb to the substrate surface. However, for near-field optical CVD (NFO CVD), photodissociation can take place even in nonresonant conditions, due to the inherent properties of the optical near field. In this letter, we examine the NFO CVD of nanometric Zn dots in nonresonant conditions. This technique makes it possible to use various light sources and gas sources for the deposition of a variety of nanometric materials.

Figure 1 shows the experimental setup for NFO CVD. Ultra-high-purity argon (Ar) was used as a buffer gas and diethylzinc (DEZn) as a reacting molecular gas source. The second harmonic ($\lambda = 244\,\mathrm{nm}$) of an Ar^+ laser was used as a light source that resonates the absorption band of DEZn.[7] The fundamental frequencies of $Ar^+(\lambda = 488\,\mathrm{nm})$ and He–Ne($\lambda = 633\,\mathrm{nm}$) lasers were used as nonresonant light sources. The fiber probe used for NFO CVD was a high-throughput single tapered UV fiber probe, which was fabricated by pulling and etching a pure silica core fiber.[1] The cone angle of the fabricated fiber probe was 30° and its apex diameter was 30 nm. In order to investigate the deposition effect of nonresonant far-field light, a fiber probe without the usual metal coating, i.e., a bare fiber probe, was used for the deposition. Therefore, the optical far field was generated by light leaking through the circumference of the fiber probe, while the optical near field was generated at the apex, as shown in Fig. 1. The separation between the fiber probe and the sapphire substrate was controlled to within several nanometers by using a shear-force technique.[1] The laser output power from the fiber probe was measured with a photodiode placed behind the sapphire substrate. The sizes of the deposited Zn dots were measured using a shear-force microscope. During deposition, the partial pressure of DEZn was 100 mTorr and the total pressure in the chamber was 3 Torr. Details of the Zn deposition procedures have been reported in a previous work.[5] It should be noted that the deposition of Zn on the fiber probe and the resultant decrease in the efficiency of optical near-field generation are negligible because the deposition time is sufficiently short, as has been pointed out elsewhere.[5,8]

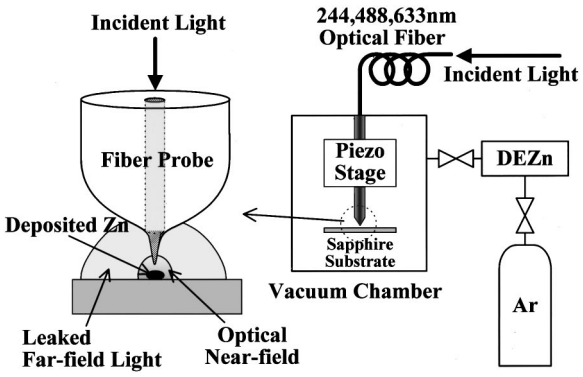

FIG. 1. Experimental setup for chemical-vapor deposition using an optical near field.

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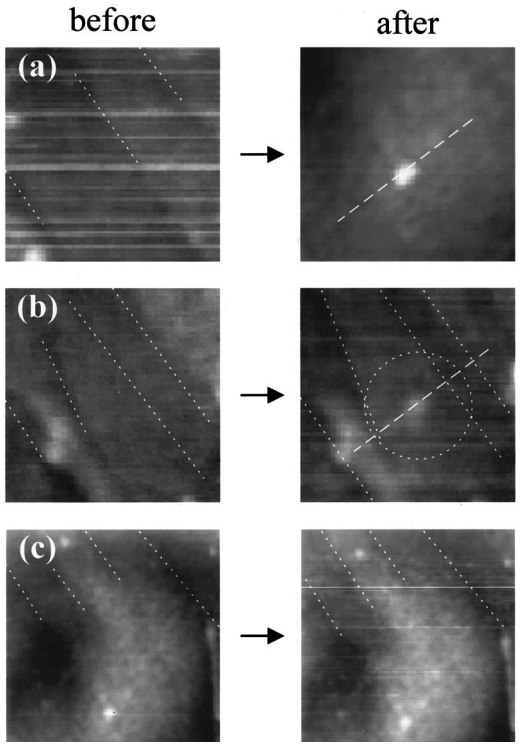

FIG. 2. Shear-force topographical images before and after NFO CVD at wavelengths of $\lambda = 244$ (a), 488 (b), and 633 (c) nm. The image sizes are 300×300 nm. The observed laser output power and the irradiation time for deposition were 1.6 μW and 60 s (a), 150 μW and 75 s (b), and 240 μW and 300 s (c).

Figure 2 shows the shear-force topographical images before and after NFO CVD on the sapphire substrate with atomic-level steps[9] for $\lambda = 244$ (a), 488 (b), and 633 (c) nm. For Fig. 2(a) ($\lambda = 244$ nm), the laser power was 1.6 μW and the irradiation time was 60 s. Atomic-level step structures 0.4 nm high on the sapphire substrate are clearly observed, as indicated by the dashed lines in the left-hand side of Fig. 2(a) (before the NFO CVD). However, after the NFO CVD (right-hand side), the atomic-level steps disappear and a deposited Zn dot less than 50 nm in diameter appears at the center of the image. This occurs because the optical near field deposited the Zn dot directly under the apex of the fiber probe. Furthermore, since the bare fiber probe also leaked strong far-field light, a Zn layer that covered the atomic-step structures was deposited.

For Fig. 2(b), the laser power was 150 μW and the irradiation time was 75 s. The photon energy at this wavelength ($\lambda = 488$ nm) is higher than the dissociation energy of DEZn, but it is still lower than the absorption edge of DEZn.[7,10] Therefore, it is not absorbed by the DEZn gas. A Zn dot less than 50 nm in diameter appears at the center of the broken circle on the right-hand side of Fig. 2(b). The atomic-level steps in Fig. 2(b) are still observed, despite the leakage of far-field light from the bare fiber probe.

In Fig. 2(c) ($\lambda = 633$ nm), the laser power was 240 μW and the irradiation time was 300 s. Despite the higher power and longer irradiation time, there was no Zn deposition. This shows that the thermal effect of laser irradiation is negligible for Zn deposition.

In Fig. 3, the solid curve is a cross-sectional profile of the Zn dot deposited at 488 nm across the dashed line in Fig.

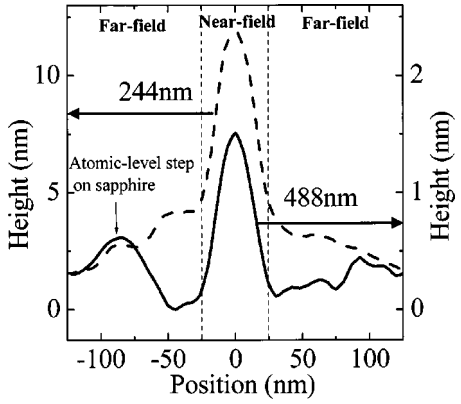

FIG. 3. Cross-sectional profiles of the deposited Zn patterns. Dashed and solid curves represent profiles along the dashed lines on the right-hand side of Figs. 2(a) and 2(b), respectively.

2(b). The dashed curve represents the cross-sectional profile of the Zn dot deposited at $\lambda = 244$ nm, taken across the dashed line in Fig. 2(a). These curves confirm that Zn dots with a full width at a half maximum of 30 nm were deposited in the region where the optical near field is dominant. The dashed curve has tails 4 nm high on both sides of the dot. These tails correspond to the deposition by the leaked far-field light. The solid curve has no tails; thus, it is clear that the leaked 488 nm far-field light did not deposit a Zn layer. This result agrees with previous work using conventional optical CVD for Zn deposition with a far-field light with $\lambda = 300$ nm.[11] It should be noted that the 30 nm Zn dot without tails was deposited under a nonresonant condition, despite the presence of leaked far-field light.

We now discuss the possible mechanisms of DEZn dissociation by the nonresonant optical near field. Figure 4 shows potential curves of an electron in the DEZn molecular orbital drawn as a function of the internuclear distance of a C–Zn bond, which is involved in photodissociation.[7] The relevant energy levels of the molecular vibration mode are also represented by horizontal lines in each potential curve. When using a conventional far-field light, photoabsorption (indicated by a white arrow in Fig. 4) dissociates DEZn.[12] In contrast, there are three possible mechanisms of photodissociation using a nonresonant optical near field. The first is the two-photon absorption process, as indicated by the two arrows ① in Fig. 4, due to the high-energy density of the

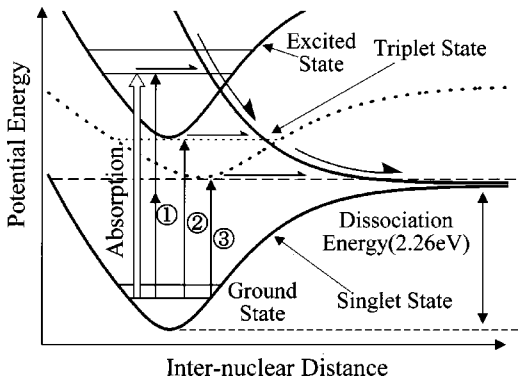

FIG. 4. Potential curves of an electron in DEZn molecular orbitals. The relevant energy levels of the molecular vibration modes are also represented by horizontal lines.

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optical near field at the apex of the high-throughput fiber probe. The second is the transition, shown by arrow ②, to the intermediate-energy level (dotted curve) induced by the fiber probe and successive relaxation to the dissociative triplet state. Such an induced transition is due to energy transfer between two localized dipole oscillators, i.e., the near-field probe and the DEZn molecules. Similar energy transfer has been observed between optically forbidden levels in dye molecules.[13] The third mechanism involves the transition to an excited state of a molecular vibration mode whose energy is higher than the dissociation energy (2.26 eV), as indicated by the dashed line and arrow ③ in Fig. 4. Although this transition is prohibited by the wave-number conservation law for conventional far-field light,[14] it is allowed in the present case because of the large uncertainty in the wave number of the sub-wavelength-size optical near field. The three mechanisms mentioned above are not adopted when $\lambda = 633\,\mathrm{nm}$ light is used, because its photon energy is lower than the dissociation energy of DEZn and its two-photon energy is also lower than the energy at the absorption edge. This is confirmed by Fig. 2(c).

The experimental results and the suggested mechanisms described above show numerous potential advantages, i.e., this technique not only increases spatial selectivity, but also makes it possible to use various light sources and gas sources not previously used in conventional far-field optical CVD. Thus, nonresonant NFO CVD is a very useful nanofabrication technique.

In conclusion, we demonstrated the deposition of a 30 nm Zn dot using NFO CVD with nonresonant light and discussed the possible mechanisms of deposition. Details of these mechanisms are under investigation, which involves evaluating the dependence of the deposition rate on the optical near-field energy density, the probe–substrate separation, photon energy, and so on.

[1] M. Ohtsu, *Near-Field Nano/Atom Optics and Technology* (Springer, Tokyo, 1998).
[2] M. Ohtsu, Tech. Dig. Ser.-Opt. Soc. Am. **3749**, 478 (1999).
[3] V. V. Polonski, Y. Yamamoto, M. Kourogi, H. Fukuda, and M. Ohtsu, J. Microsc. **194**, 545 (1999).
[4] V. V. Polonski, Y. Yamamoto, J. D. White, M. Kourogi, and M. Ohtsu, Jpn. J. Appl. Phys., Part 2 **38**, L826 (1999).
[5] Y. Yamamoto, M. Kourogi, M. Ohtsu, V. Polonski, and G. H. Lee, Appl. Phys. Lett. **76**, 2173 (2000).
[6] J. G. Calvert and J. N. Patts, Jr., *Photochemistry* (Wiley, New York, 1966).
[7] R. L. Jackson, J. Chem. Phys. **96**, 5938 (1992).
[8] M. Ohtsu, K. Kobayashi, H. Ito, and G. Lee, Proc. IEEE **88**, 1499 (2000).
[9] M. Yoshimoto, T. Maeda, T. Ohnishi, H. Koinuma, O. Ishiyama, M. Shinohara, M. Kubo, R. Miura, and A. Miyamoto, Appl. Phys. Lett. **67**, 2615 (1995).
[10] R. L. Jackson, Chem. Phys. Lett. **163**, 315 (1989).
[11] M. Shimizu, H. Kamei, M. Tanizawa, T. Shiosaki, and A. Kawabata, J. Cryst. Growth **89**, 365 (1988).
[12] H. Okabe, *Photochemistry* (Wiley, New York, 1978).
[13] H. Sumi, J. Phys. Chem. B **103**, 252 (1999).
[14] M. Balkanski, *Optical Properties in Solid, Handbook on Semiconductors* (North-Holland, Amsterdam, 1980), Vol. 2.

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