

Photochemical vapour deposition employing optical near field

In photochemical vapour deposition, particles or films are deposited on a substrate by organic molecules. It is essential that the organic molecules be photo-dissociating. The present lecture deals with the conventional photochemical vapour deposition process, its disadvantage and the advantages of using photochemical vapour deposition employing the concept of dressed photon-coherent phonon fabrication technique.

1 Adiabatic photochemical vapour deposition

Conventional photochemical vapour deposition involves the principle of adiabatic nanofabrication where propagating light resonates the absorption band of metal-organic vapour. An important point to note is that the photon energy of the light source should be much greater than that of dissociation energy. The entire procedure of the conventional photochemical vapour deposition can be subdivided into two halves:

1. One that involves gas-phase photo dissociation where the molecules are excited from the ground state to the excited electronic state by the resonant photons;
2. After the excited molecules undergo relaxation process and go to the dissociation channel, they constitute as dissociated metallic atoms. Finally, they get adsorbed to the substrate

1.1 Adiabatic excitation process

Let $|g\rangle|e\rangle$ represent the electronic ground state and let $|e_l\rangle|e_{vib}\rangle$ represent the vibrational energy state of a given molecule. At room temperature the molecule remains stable in the lowest energy state denoted by $|g\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$. Now if $|e_h\rangle|e_{vib}\rangle$ represents a higher vibrational energy state of the molecule, when the molecule is excited from the stable lowest energy state $|g\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$ to a stable, say, $|g\rangle|e\rangle \otimes |e_h\rangle|e_{vib}\rangle$, whose energy is greater than the dissociation energy E_{dis} , the molecule is said to be dissociated. But in reality, such a transition will not take place from the ground energy state $|g\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$ to the excitation energy state $|g\rangle|e\rangle \otimes |e_h\rangle|e_{vib}\rangle$. This is due to the fact that $|g\rangle|e\rangle \otimes |e_h\rangle|e_{vib}\rangle$ happens to be an electric dipole forbidden energy state. Moreover, only when a given molecule can be heated an extremely high temperature, will thermal excitation take place for the molecule to get dissociated. Let $|e_{ex}\rangle|e\rangle$ denote an allowed excitation energy state whose energy is much higher than the dissociation energy. In that case, the molecule can easily get optically excited from the electronic ground state $|g\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$ to the electronic excited state $|e_{ex}\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$, as it is an electric dipole allowed energy transition. During this electric dipole allowed energy transition, the heavy nuclei of the given molecule stay in the lowest vibrational state. Hence the vibrational motions of the heavy nuclei do not get excited, thereby making the transition an electric dipole allowed energy transition. This excitation process is called adiabatic excitation.

1.2 Principle of conventional photochemical vapour deposition

Conventional photochemical vapour deposition takes place in an adiabatic manner as outlined above. The principle of conventional photochemical vapour deposition can be best

explained by considering the example of metallic zinc deposition, which usually employs gaseous diethylzinc, a metal organic molecule. It is observed that the photo-absorption energy E_{abs} of diethylzinc is greater than its dissociation energy E_{dis} . Hence for adiabatic photochemical vapour deposition to take place in diethylzinc, a short wavelength light whose photon energy is greater than the absorption energy E_{abs} of diethylzinc is very much required. This corresponds to the energy difference between the electronic excited state $|e_{ex}\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$ and the electronic ground state $|g\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$ of diethylzinc. As mentioned above, the vibrational motions of the heavy nuclei of diethylzinc are not excited and hence these nuclei stay in the lowest vibrational state, thereby making the transition an electric-dipole allowed energy transition. Once the diethylzinc molecule gets excited to the state $|e_{ex}\rangle|e\rangle \otimes |e_l\rangle|e_{vib}\rangle$ by absorbing the above mentioned photon, it transits to the triplet state. Due to this transition, the inter-nuclear distance of diethylzinc molecule increases from a finite value to infinity. Thus, finally, the diethylzinc molecule gets dissociated diethylzinc molecule gets deposited on the substrate by adiabatic process.

1.3 Disadvantage of conventional photochemical vapour deposition

The principle of conventional photochemical vapour deposition is outlined above. One important point to note is that conventional photochemical vapour deposition involves adiabatic excitation process, wherein organo metallic molecular vapours get dissociated due to the photochemical reaction with the far field light. Hence conventional photochemical vapour deposition technique can be employed as long as the material size is of the order of the wavelength of light. But if the material size happens to be smaller than the wavelength of propagating light, diffraction limit sets in thereby rendering the conventional photochemical vapour deposition process futile. Adiabatic photochemical vapour deposition cannot be employed for sub wavelength sized materials due to diffraction limit. Thus an advanced nanofabrication technique is very much called for which should not only realize high spatial resolution, but also should offer high precision for controlling the size and position of nanoparticles, applicable to a plethora of nanomaterials. Even though several methods such as self-organized growth method for nanofabrication, site control of substrate such as e-beam method, surface modification method and in-situ patterning of nanostructures using scanning probe method, etc., have been used extensively, all of them suffer a severe drawback such that they limit the type of materials that can be deposited. For example, the in-situ patterning method cannot be used for the case of insulators. The main culprit is the use of conventional propagating light which causes diffraction limit that does not allow the deposition of sub wavelength-sized materials. This disadvantage very much calls for a photochemical vapour deposition process that can enable the deposition of sub wavelength-sized materials and hence usher in a plethora of innovative nanofabrication techniques.

2 Non-adiabatic phonon-assisted photochemical vapour deposition

Ohtsu research group have come up with an innovative nanofabrication technique that can not only realize high spatial resolution, but also provide high resolution in controlling the size and position of various nanoparticles and hence become applicable for various types of materials including insulators. They employ the principle of optical near field technology where the optical near field allows electric dipole forbidden energy transitions, thereby enhancing the spatial resolution capability of the optical near field. Such a process is called non-adiabatic process.

2.1 Principle of non-adiabatic photochemical vapour deposition

The principle of non-adiabatic photochemical vapour deposition can be best explained by considering the deposition of diethylzinc dots whose sizes are much less than 50nm . Due to optical near field, electric-dipole forbidden energy transitions also occur, which enhances photo dissociation process by making possible four mechanisms such as (a) two-photon absorption process, (b) transition to the intermediate energy level, (c) transition to an excited state of a molecular vibration mode and (d) direct transition from the singlet ground state to the dissociative triplet state.

2.1.1 Two photon absorption process

Optical near field develops high energy density for the fiber probe which has high throughput at its apex end. This makes two photon absorption process to physically take place which cannot be accomplished by conventional photochemical vapour deposition process.

2.1.2 Transition to an intermediate energy level

Due to optical near field interaction between the relevant nanoscopic diethylzinc molecules with the irrelevant macroscopic fiber probe, the excitation levels in the diethylzinc molecules get shifted, thereby inducing intermediate excitation energy levels. Hence the molecules transit to the induced intermediate energy level and undergo successive relaxation to the dissociative triplet state. Again, due to high energy density, excitation energy levels that were once forbidden, now become active, thereby allowing optical forbidden excitation energy level transitions to occur.

2.1.3 Transition to an excited state of a molecular vibration mode

Due to optical near field, large uncertainty occurs in the wave number of the optical near field. This makes possible the transition to the excited state of the vibrational mode of the diethylzinc molecule as its energy is higher than the dissociation energy. This rare feat is not possible in the case of conventional photochemical vapour deposition technique due to the wave number conservation law for the conventional far field.

2.1.4 Direct transition

Due to Frank-Condon principle, a spatially homogeneous far-field light can only interact with electrons and not with the polarization of a diethylzinc molecule. Hence direct transition from a singlet state to a triplet state is forbidden in the case of conventional photochemical vapour deposition technique. On the other hand, an optical near field can easily interact with the polarization of the diethylzinc molecule. This is due to the fact that an optical near field has an extremely large spatial gradient occurring with a nanometric decay length. As a result, atoms in the diethylzinc molecule can be translated directly from the singlet state to the triplet state and hence get dissociated.

3 Additional reading and references

1. M. Ohtsu, K. Kobayashi, T. Kawazoe and T. Yatsui, Principles of Nanophotonics (CRC Press, New York, 2008).
2. M. Ohtsu (Ed.), Progress in Nanophotonics 1 (Springer-Verlag, Berlin, 2011).

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