Facile Fabrication Procedure for C_{60}-Doped Silicon Oxide Thin Films

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C_{60}-doped silicon oxide thin films can be prepared easily by sol-gel processing using a mixture of phenyltriethoxysilane and tetraethoxysilane as the silicon oxide sources. Preparation of C_{60}-dissolved single-phase starting solutions is practicable by employing phenyltriethoxysilane which acts as a solubilization agent of C_{60} as well as the silicon oxide source.

Since the discovery of buckminsterfullerene, a wide variety of its remarkable properties have been reported.[1-5] Then, attempts have been made to entrap this class of compounds into inorganic hosts. Sol-gel processing has so far been applied for the entrapment,[6-8] since the processing was demonstrated to be effective for doping compounds with low thermal stability, such as organic dyes, into the inorganic hosts.[9] Film formation can also be done easily with the method.

The first effort for preparing C_{60}-doped silica films through sol-gel processing was made by Maggini *et al.*[7] Because of a low C_{60} content in the films, however, no evidence was shown for the presence of C_{60} therein. The low content was ascribed to low solubility of C_{60} in solvent. Because sol-gel reactions involve hydrolysis of raw materials (metal alkoxides and so on) by the addition of water or exposing to moisture in air, hydrophilic organic solvents such as alcohol are generally used for the reactions. Then, Maggini *et al.*[7] used C_{60} derivatives instead which are soluble in THF to dope into silicon oxide films by sol-gel method. Since main electronic properties of the C_{60} derivatives retain those of C_{60}, the C_{60} derivative-doped films would show similar properties to those of C_{60}-doped films. However, an additional, troublesome step for derivatizing C_{60} is necessary in this process. Consequently, this study has been aimed at devising a synthesis procedure to entrap C_{60} itself in silicon oxide films by sol-gel processing.

We used phenyltriethoxysilane [$C_6H_5Si(OC_2H_5)_3$, PTEOS] and tetraethoxysilane [$Si(OC_2H_5)_4$, TEOS] as silicon oxide sources, a mixture of toluene and ethanol as solvent, and hydrochloric acid as catalyst for promoting hydrolysis and polymerization of the alkoxysilanes. Starting solutions were prepared by adding PTEOS, TEOS, hydrochloric acid, and ethanol (4 cm^3) to a toluene (10 cm^3) solution of C_{60} (0.005 g). A (PTEOS + TEOS):C_{60}:H_2O:HCl molar ratio of the solutions was fixed at $1.00{:}1\times10^{-3}{:}3.00{:}0.05$, and a PTEOS:TEOS molar ratio at 2.0:1.0.

The solutions consisted of a single phase, which were stirred for 1 d in the closed vessel at room temperature, and then soaked at 40 °C under stirring with the cap of the vessel open. The viscosity of the solutions increased with time. Transparent films with a magenta color could be fabricated onto glass substrates from the viscous solutions by spinning.

Figure 1 (a) shows the UV-VIS spectrum of the film which was prepared by twice coating with the solution and drying at 50 °C in air to remove the solvent and low-boiling components, whereas that of the film prepared from a C_{60}-free solution of PTEOS and TEOS in the same manner is shown in Figure 1 (b). Leach *et al.*[10] described that C_{60} gives rise to bands at 328.4 and 256.6 nm, which are due to transitions to the 3^1T_{1u} and 6^1T_{1u} excited states, respectively, from the measurement of hexane solutions of C_{60}. Several bands at 250-270 nm in Figure 1 (b) can be assigned to the C_6H_5-Si group in the silicon oxide film formed from PTEOS.[11] Because of the overlap with these bands, the band due to the transition to the 6^1T_{1u} state of C_{60} cannot clearly observed in Figure 1 (a). However, a broad band is seen centered around 338 nm distinctly. Its wavelength is slightly higher than that due to the transition to the 3^1T_{1u} state of C_{60} observed for the hexane solutions. Maggini *et al.*[7] described that bands due to the C_{60} derivatives in the films appear at *ca.* 269 and 336 nm, and attributed such shifts to higher wavelengths to difference in the state of the C_{60} derivatives in the films and the solutions. Dai *et al.*[6] reported such red-shifts on C_{70} entrapped in silica gel as well. From these facts, the band at *ca.* 338 nm would be assigned to the transition to the 3^1T_{1u} state of C_{60}, suggesting that C_{60} is embedded in the film.

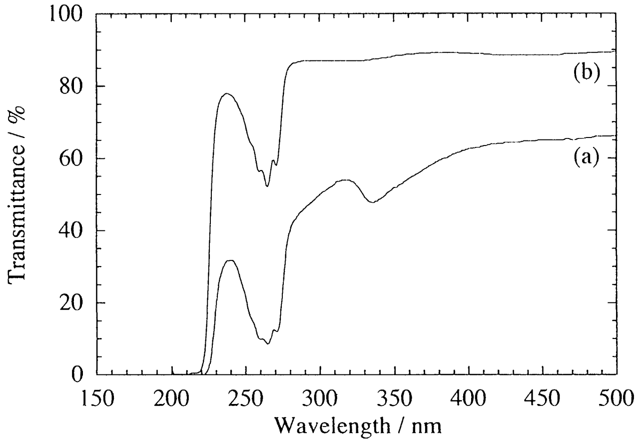

Figure 1. The UV-VIS spectra of (a) C_{60}-doped and (b) C_{60}-undoped silicon oxide films prepared using PTEOS and TEOS as the silicon oxide sources by sol-gel processing.

In the photoluminescence spectrum of the C_{60}-doped film measured using an Ar^+ laser at an excitation wavelength of 488 nm, two peaks due to C_{60} are observed at 1.59 and 1.73 eV [Figure 2 (b)]. These positions are slightly higher than those observed for C_{60} films which we prepared by vapor deposition (1.58 and 1.66 eV) [Figure 2 (a)]. The shifts may result from the quantum size effect of C_{60} embedded in the film. On the basis of the square-well potential, the width of the space where C_{60} is present is calculated to 7.15 nm from the shifts. Thus, C_{60} in the sol-gel derived film is estimated to be present as small clusters probably comprised of *ca.* 10 C_{60} molecules.

No single-phase starting solution with the composition could

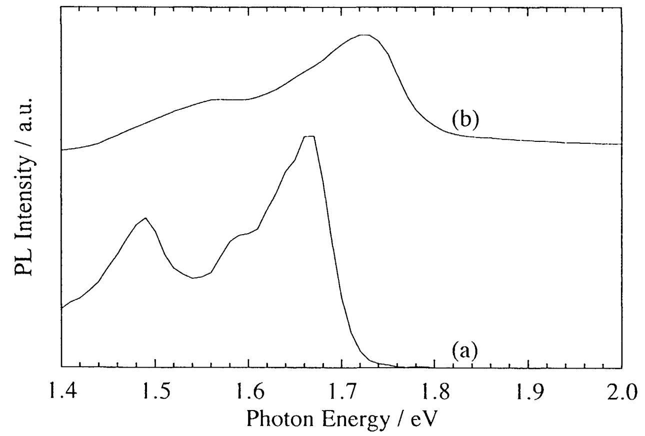

Figure 2. The photoluminescence spectra of (a) a C_{60}-vapor deposition film and (b) a C_{60}-doped silicon oxide film measured at 50 K.

not be prepared using TEOS solely as the silicon oxide source. Then, PTEOS was applied as the source, since C_{60} is soluble in organic solvents with the benzene ring such as toluene. On the other hand, opaque films were obtained from starting solutions prepared using PTEOS solely. Transparent films could be prepared only when both of TEOS and PTEOS was used as the silicon oxide sources. Minami and Tohge[12] demonstrated earlier that combination use of tri- and tetrafunctional alkoxysilanes leads to the formation of transparent silicon oxide films.

Additionally, the stir of the solutions in the closed vessel for 1 d is necessary for preparing the viscous solutions suitable for coating. When the solutions were soaked at 40 °C in the open system from the beginning, that is, without stirring in the closed system at room temperature for 1 d, C_{60} precipitated out with decreasing amount of the solvent, meaning the stir in the closed system is necessary. Trimethylsilylation technique combined with gel permeation chromatography[13] indicated the formation of siloxane compounds with the molecular weight of *ca.* 1100 as the trimethylsilyl derivatives in the solution after 1 d of stir in the closed system. Such oligomeric siloxane species would be easy to entrap C_{60} upon further polymerization, which would prevent from the precipitation of C_{60}. On the basis of this procedure, single-phase starting solutions with a (PTEOS + TEOS):C_{60}:H_2O:HCl molar ratio of $1.00:5\times10^{-3}:3.00:0.05$, in which the C_{60} content is five times larger than that of the solutions described above, could also be prepared, from which C_{60}-doped films with a larger C_{60} content could be synthesized by spin-coating.

In conclusion, silicon oxide films in which C_{60} was doped as small clusters could be produced easily by sol-gel processing. The salient feature of this procedure is the use of PTEOS as both a solubilization agent of C_{60} and a silicon oxide source. Further study on the properties of the films are now under study.

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