Structural evolution of silicone oil liquid exposed to Ar plasma*

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Structure properties of silicone oil serving as a liquid substrate exposed to Ar plasma are investigated in this paper. Under the action of energetic Ar ions, the surface of silicone oil liquid substrate exhibits a branch-like fractal aggregation structure, which is related to the structure evolution of silicone oil liquid from Si–O chain to Si–O network. The radicals from the dissociation of silicone oil molecule into the Ar plasma turns the plasma into a reactive environment. Therefore, the structural evolution of silicone oil liquid substrate and the reactive radicals in the plasma space become possible factors to affect the aggregation of nanoparticles and also the structures and the compositions of nanoparticles.

Keywords: silicone oil liquid substrate, structure evolution, Ar plasma

PACC: 5240, 6120N, 5280P

1. Introduction

Ultrafine metal nanoparticles are of interest for their size-dependent photonic and electronic properties.[1] To obtain the size-controllable, clean and byproductfree nanoparticles, the deposition of ultrafine metal nanoparticles on the low-vapour-pressure liquid surface is receiving increasing attention.[1−5] With the development of plasma technology, the plasma has been widely used in material processing.[6−9] Therefore, the silicone oil and ionic liquid have been used as the liquid substrates in the plasma to deposit the iron (Fe), silver (Ag) and gold (Au) nanoparticles,[1−3] and the Fe thin films on it.[4−5] The aggregations of Ag and Fe clusters with the branch or disk-shape patterns were obtained,[2,5] and the decreasing of Au nanoparticle size was also observed.[1] Due to the fact that different aggregation behaviours can lead to a difference in material property,[10,11] the controlling of the particles aggregation is very important for preparing the nanoparticles. Usually, the difference in aggregation behaviour is mainly attributed to a difference in the processing parameter. The effect of liquid surface state on particle aggregation has received little attention. Zhang *et al.*[5] found that the wavy buckles appeared at a higher sputtering power or a long deposition time, and attributed them to the formation of a soft polymer layer at the top surface of silicone oil, however, no further evidence was given.

Usually, the aggregation of nanoparticles on the liquid surface is by a random walk motion due to statistical fluctuations in their momentum by collisions with liquid molecules.[2] According to the theory of Brownian motion, for a two-dimensional motion the mean square displacement $\langle \Delta r^2 \rangle$ of particle migrations is given by[2]

$$\langle \Delta r^2 \rangle = 4kTF^{-1}\Delta t, \tag{1}$$

where k is the Boltzmann constant, T is the temperature, Δt is the time, and F is the friction coefficient. Therefore, the aggregation of nanoparticles on the liquid surface depends on the friction coefficient, temperature and time. The silicone oil is a viscous liquid and its viscous coefficient depends on the number n of $-[(CH_3)_2SiO]_n-$ chains.[12] When the silicone oil is exposed to plasma, its structural property is one of the most important factors for the liquid substrate application. During depositing nanoparticles on silicone oil liquid substrate, the interactions between plasma and silicone oil liquid, especially the bombardment of energetic ions on the liquid, may lead to the structure change of silicone oil liquid and the temperature

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fluctuation at liquid surface. As a result, the aggregation behaviour of nanoparticles on silicone oil liquid will be influenced. However, the structural property of silicone oil liquid, when it is exposed to Ar plasma, is seldom reported. The structure properties of silicone oil exposed to Ar plasma are investigated in the present paper.

2. Experiment

In the experiment, the silicone oil liquid substrates with a viscous coefficient of 20 $mm^2 \cdot s^{-1}$ and a thickness of 0.5 mm were obtained using a spin-on method at 4500 rpm. Then the liquid substrates were treated in an argon (Ar) 60 MHz/2 MHz dual-frequency capacitively coupled plasma (DF–CCP) system as shown in Fig. 1.[13] In the DF–CCP system, the decoupling of two sources made the plasma density and ions energy controlled independently by the high-frequency (HF) and the low-frequency (LF) powers separately.[14,15] The HF power of 50 W was applied to the top electrode to produce plasma. The silicone oil liquid substrates were placed at the bottom electrode to which an LF power of 10 W to 20 W was applied, thereby changing the energies of ions reaching the silicone oil substrates. Therefore, the structural evolution of liquid substrates was mainly induced by energetic Ar ions. The diameters of two symmetrical electrodes were both 200 mm and the spacing between two electrodes was 50 mm. The base pressure reached 5×10^{-4} Pa and the discharge pressure was kept at 50 Pa with an Ar flow rate of 10 sccm. The treatment time was 15 min.

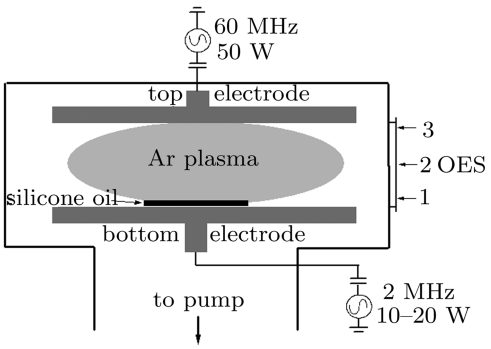


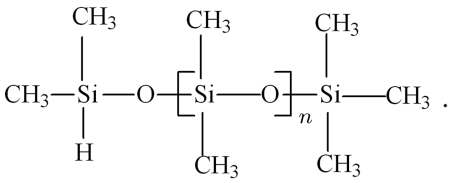
Fig. 1. Schematic diagram of dual-frequency capacitively coupled plasma system.

The microstructure of silicone oil liquid was observed using a Hitachi S570 scanning electron microscopy. The bonding configurations of silicone oil liquid were characterized by a JASCO 600 Plus Fourier transform infrared (FTIR) spectroscopy in a wavenumber range of 600–4000 cm^{-1} with a resolution of 3 cm^{-1}. Meanwhile, the excited radicals in the spatial plasma were measured using optical emission spectroscopy (OES) (AvaSpec-2048 fibre optic spectrometer). The optical emission signals in a wavelength range of 200–800 nm with a resolution of 0.05–0.13 nm were collected via a fibre located, separately, at approximately 5 mm above the surface of silicone oil liquid substrate (position 1), in the centre of bulk plasma (position 2) and at 5 mm below the surface of top electrode (position 3). The relative density of radicals was calculated from the emission line intensity ratio of excited radical to Ar (750.4 nm) radical.

3. Results and discussion

Figure 2(a) shows the morphology of untreated silicone oil liquid substrate. Its surface can be seen to be smooth. After treating it by Ar plasma at an LF power of 20 W, the surface turns out to consist of a branch-like fractal structure and is rougher as shown in Fig. 2(b). Because the fractal growth in silicone oil, soft matter, depends mainly on thermal fluctuation,[16] the morphology change of silicone oil surface is related to the thermal fluctuation due to the Ar ion bombardment.

Figure 3 shows the FTIR spectra of silicone oil liquid. For the untreated silicone oil, the bonding configurations include two splitting Si–O–Si peaks (1012 cm^{-1} and 1115 cm^{-1}) in Si–O chain, CH_3 radicals in $SiMe_x$ (1261 cm^{-1}) and in $SiMe_2$ (754 cm^{-1}), C–H_3 (1413 cm^{-1}, 1446 cm^{-1}, 2905 cm^{-1} and 2963 cm^{-1}), C–H (688 cm^{-1} and 703 cm^{-1}), the H–Si–O (865 cm^{-1}), Si–O (794 cm^{-1}, 810 cm^{-1} and 823 cm^{-1}), and Si–H (664 cm^{-1} and 842 cm^{-1}). According to the FTIR results, the structural formula of the silicone oil molecule is expressed as follows:



(2)

After the Ar plasma treatment at an LF power of 10 W, the bonding configurations of silicon oil liquid still include Si–O–Si (1012 cm^{-1} and 1103 cm^{-1}), CH_3 radicals in $SiMe_x$ (1261 cm^{-1}) and in $SiMe_2$ (754 cm^{-1}), C–H_3 (1413 cm^{-1}, 1446 cm^{-1}, 2905 cm^{-1} and 2963 cm^{-1}), and Si–O (794 cm^{-1} and 810 cm^{-1}).

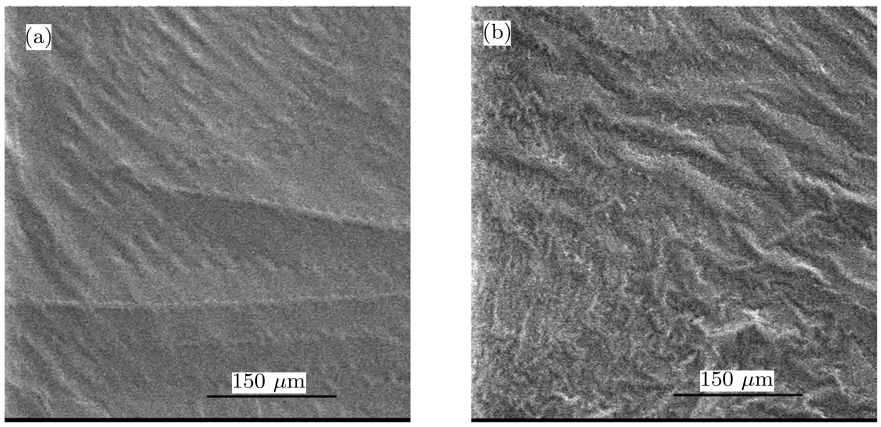
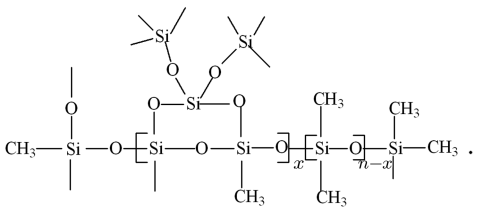


Fig. 2. Morphologies of (a) silicone oil and (b) silicone oil liquid substrate treated by Ar plasma at an LF power of 20 W.

The absorptions of H–Si–O (865 cm^{-1}) and Si–H (664 cm^{-1} and 842 cm^{-1}) decrease obviously. With LF power increasing to 20 W, the blue-shift from 1012 cm^{-1} to 1024 cm^{-1} and the red-shift from 1103 cm^{-1} to 1090 cm^{-1} of Si–O–Si absorptions appear. The absorptions from CH_3 radicals, C–H_3, H–Si–O and Si–H decrease greatly. Due to the Si–O–Si absorptions at 1024 cm^{-1} and 1090 cm^{-1} from the Si–O network, especially at 1024 cm^{-1} from the three-fold Si–O ring, the results indicate that Si–O network and Si–O ring have formed in the silicone oil liquid. The possible structural change of silicone oil liquid is shown as follows:



(3)

Therefore, the Ar plasma treatment at a higher LF power leads silicone oil liquid to obviously change its structure.

Because the increasing of LF power in DF–CCP mainly increases the ion energy,[15] the structural change of silicone oil liquid at higher LF powers is related to the role of energetic Ar ions. The bombardment of energetic Ar ions leads to the removing of CH_x and H radicals by breaking Si–CH_3 and Si–H bonds. The linkage between leaving Si and O forms the Si–O network, thereby producing more Si–O chain linkages. As a result, a branch-like fractal Si–O network forms in the treated silicone oil liquid.

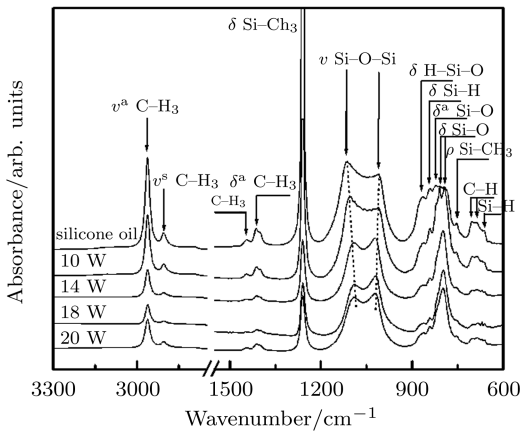


Fig. 3. FTIR spectra of silicone oil and silicon oil liquid substrate treated by Ar plasma at LF powers of 10, 14, 18 and 20 W separately.

The interaction between Ar plasma and silicone oil not only changes the liquid surface state and bonding configurations, but may also influence the compositions in the spatial plasma. Therefore, the excited radicals in the plasma were measured by optical emission spectroscopy. The typical optical emission spectra of plasma at the HF power of 50 W and the LF power of 20 W are shown in Fig. 4. In the spectra, except the Ar excited lines, the excited lines from C (387.97 nm),[17] SiH (413.19 nm),[18] SiO (423.75 nm),[19] CH (430.05 nm),[20] Si (591.15 nm),[21] H_2 (603.16 nm),[22] O (604.31 nm),[23] and H_α (656.28 nm)[24] radicals are

also observed. The relative densities of Si, O and H radicals at different spatial positions and different LF powers are shown in Fig. 5. It can be seen that there exist these reactive radicals in the plasma space though their relative densities are different. The results indicate that the radicals originate from the dissociation of the silicone oil molecule into the Ar plasma, which makes the plasma compositions more complex. During depositing metal nanoparticles by sputtering, the metal particles from the target may react with the reactive radicals of silicone oil molecule dissociated into the plasma space. As a result, the structures and the compositions of nanoparticles deposited on the liquid substrate may be affected.

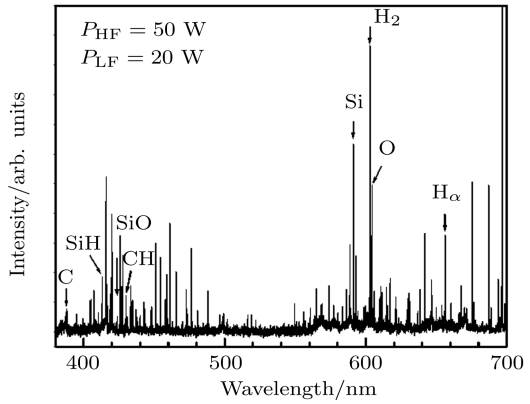


Fig. 4. Optical emission spectra of the plasma compositions when the silicone oil liquid substrate is exposed to Ar plasma.

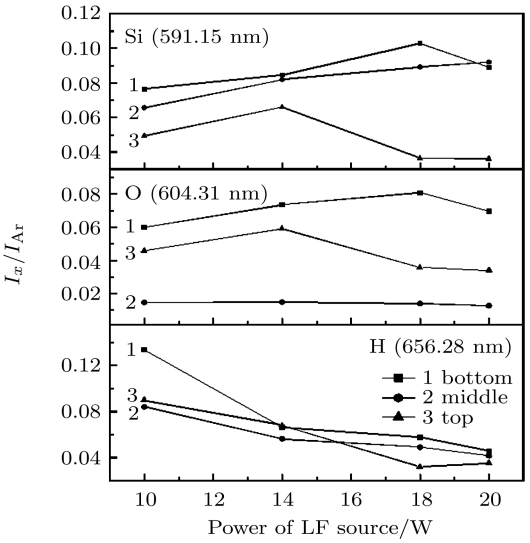


Fig. 5. Dependences of the relative density I_x/I_{Ar} of Si, O and H radicals on LF power at different spatial positions.

4. Conclusions

The structure properties of silicone oil serving as a liquid substrate exposed to Ar plasma are investigated. Under the action of energetic Ar ions, the surface of silicone oil liquid substrate exhibits a branch-like fractal aggregation structure, which is related to the structure evolution of silicone oil molecule from Si–O chain to Si–O network. The radicals from the dissociation of silicone oil molecule into the Ar plasma turn the plasma into a reactive environment. Therefore, the structural evolution of silicone oil liquid substrate and the reactive radicals in the plasma space are the possible factors affecting the aggregation of nanoparticles and also the structures and the compositions of nanoparticles.

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