Rapid transport of nano-particles in amplitude modulated rf discharges for depositing porous ultra-low-k films

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Abstract. We have proposed a novel one-step method for synthesizing nano-particle composite porous low-k films. For the method, nano-particles as nano-building blocks and radicals as adhesives are produced in reactive discharge plasmas; both of them are transported to a substrate; and eventually nano-particles are co-deposited there together with radicals. Size of nano-particles is controlled by the duration of pulse rf discharge; their rapid transport of a velocity more than 60 cm/s is realized by pulse rf discharges with an amplitude modulation (AM) of the discharge voltage. The deposition rate with AM is 0.65 nm/s, which is 7 times as high as that without AM, while dielectric constant k =1.1-1.4 and porosity =60-63 % of the films with AM are nearly equal to those without AM. Therefore deposition of porous low-k films using pulse rf discharges with AM is a promising method for increasing the deposition rate without varying the properties of films.

1. Introduction
The increase of the integration density and of the operation speed in ultra-large-scale integrated microelectronics requires a reduction in the dielectric constant for high-frequency insulation between the copper connections of some tenth-of-micrometer thickness [1]. Recently, the quality of the dielectric has been defined by its dielectric constant k (> 1) relative to the unpolarized vacuum (k = 1). Bulk low-k will never reach k lower than 3 and the only way to achieve a further decrease in k is to introduce nanoporous dielectric films compatible with the required mechanical behavior [2]. For synthesizing ultra porous low-k films having sufficient mechanical strength, we have proposed a novel one-step method as shown in Fig. 1 [3]. For the method, nano-particles as nano-building blocks and radicals as adhesives are produced in reactive discharge plasmas; both of them are transported to a substrate; and eventually nano-particles are co-deposited there together with radicals. Therefore, control of their size as well as that of their transport from their generation region to a substrate is important to realize a tailored structure of films.

To obtain information about such nano-particle formation and transport, we have observed their behavior in pulse rf discharges without and with amplitude modulation (AM) using two-dimensional laser-light-scattering method (2DLLS). Moreover, we have deposited nano-particle composite porous ultra-low-k films using pulse rf discharges with AM to increase the deposition rate. In this paper, we describe these experimental results.
Four elementary processes
1. dissociation of ingredient gas (radical generation)
2. nano-particle formation
3. nano-particle & radical transport
4. porous film formation

Role of nano-particles and radicals
nano-particles: nano-building blocks
radicals: adhesives

Figure 1. Concept of one-step method for synthesizing nano-particle composite porous ultra-low-k films.

2. Experimental
Experiments were carried out using a capacitively coupled rf discharge reactor described elsewhere [4-7]. The reactor together with a 2DLLS system is shown in Fig. 2. A powered disc electrode 20 mm in diameter and 1 mm in thickness was set in the middle of two grounded electrodes of 60 mm diameter placed at a distance of 40 mm, in the reactor of 260 mm diameter and 230 mm height. Gas of Si(CH$_3$)$_2$(OCH$_3$)$_2$ diluted with Ar was supplied to the reactor. The flow rate of Si(CH$_3$)$_2$(OCH$_3$)$_2$ and that of Ar were 0.2 and 40 sccm, respectively. The total gas pressure was 133 Pa. The temperature of the reactor wall was kept at 358-368 K to avoid liquefaction of Si(CH$_3$)$_2$(OCH$_3$)$_2$ on the wall surface. To dissociate Si(CH$_3$)$_2$(OCH$_3$)$_2$ and generate nano-particles, we sustained a discharge by applying 816 peak-to-peak voltage of 13.56 MHz to the powered electrode for a discharging period $T_{on}$ was in a range of 0.1 to 4 s. The self-bias voltage was -350 V. The corresponding discharge power was 75 W. For an AM discharge, the discharge voltage was modulated as shown in Fig. 3. The peak-to-peak voltage $V_{AM}$ during the modulation was in a range of 816-1193 V and the modulation period $\Delta t$ was 50 ms or 100 ms.

Spatiotemporal evolution of size and density of nano-particles was measured using a 2DLLS method [8] combined with a simple method for deducing their size and density [4]. For the method, a sheet beam of YAG laser light of 1.0 W at 532 nm was passed parallel to the surface of the upper grounded electrode. The height and width of the sheet beam was 34 mm and 1 mm, respectively. The intensity of light scattered by nano-particles was detected at right angles with an ICCD camera equipped with an interference filter of a center wavelength of 532 nm and FWHM of 1 nm. The size (diameter) and density of nano-particles were deduced from their thermal coagulation that took place after turning off the discharges [4].

For deposition experiments, Si substrates were placed on the lower grounded electrode. The distance between the powered electrode and Si substrates on the lower grounded electrode was set to 9 mm, and the substrate temperature was 368 K. The dielectric constant $k$ was deduced from capacitance of a metal/insulator/metal (MIM) structure having Al electrodes measured at 100 kHz.

Figure 2. Experimental setup.

Figure 3. Envelope of discharge voltage.
3. Results and discussion

3.1. Size and density of nano-particles

Time evolution of size and density of nano-particles were deduced as shown in Fig. 4. The size linearly increases from 1 nm for the discharging period $T_{\text{on}} = 0.12$ s to 20 nm for $T_{\text{on}} = 4$ s, while the corresponding density decreases from $1 \times 10^{12}$ to $2 \times 10^{10}$ cm$^{-3}$. Thus the size can be controlled by $T_{\text{on}}$. The growth rate is 6.6 nm/s. The volume fraction of nano-particles in a unit volume increases monotonously with $T_{\text{on}}$, indicating that nano-particles grow via CVD processes on their surface during the discharging period. After turning off discharges, nano-particles grow due to their thermal coagulation, since their volume fraction is constant during the growth [4]. For synthesizing porous low-k films composed of nano-particles, such coagulation should be avoided to keep the size of nano-particles close to the value just after turning off discharges.

3.2. Transport of nano-particles in pulse rf discharges without and with AM

Figure 5 shows trajectory of nano-particles in z-direction in pulse rf discharges of $T_{\text{on}} = 4$ s without and with AM of $\Delta t = 100$ ms. Without AM nano-particles are transported from their generation region around the powered electrode towards the grounded electrode after turning off the discharge at a velocity of 6-10 cm/s, while they are transported rapidly at a velocity more than 60 cm/s with AM. Nano-particles are driven by thermophoretic force after turning off the discharge without AM, whereas they are driven by ion drag force during AM in the discharge with AM. The longer period of the modulation is needed for rapid transport for the larger nano-particles. The higher discharge voltage of the modulation is needed for rapid transport of nano-particles having a smaller mean charge. Therefore, two important parameters for the rapid transport are the discharge voltage and the period of AM.

3.3. Synthesizing porous low-k films using pulse rf discharges without and with AM

Pulse rf discharges with AM realize rapid transport of nano-particles towards a substrate as described in the previous section. Such rapid transport is required for realizing a high deposition rate of nano-particle composite porous low-k films and for suppressing their coagulation during their transport; because the deposition rate is proportional to a density $n_p$ of nano-particles and their speed $v_p$ to a substrate, while the coagulation rate of nano-particles is proportional to $n_p^2$. We deposit porous low-k films using pulse rf discharges with AM to increase the deposition rate. Table I shows some properties of porous low-k films deposited using discharges of $T_{\text{on}} = 0.3$ s without and with AM, and Figure 6 shows SEM image obtained with AM and the interval =1 s. The deposition rate with AM and the interval =1 s is 0.65 nm/s, which is 7 times as high as that without AM, and 10 times as high as that
with AM and the interval =10 s. Dielectric constant k =1.1-1.4 and porosity =60-63 % of the films with AM are nearly equal to those without AM. Therefore deposition of porous low-k films using pulse rf discharges with AM is a promising method for increasing the deposition rate without varying the properties of films.

| deposition rate | goal | without AM interval 10 s | with AM interval 10 s | with AM interval 1 s |
|----------------|------|--------------------------|----------------------|--------------------|
| k              | 2.0  | 1.2                      | 1.1                  | 1.4                |
| porosity       | 26 % | 61 %                     | 63 %                 | 60 %               |

Table I. Properties of porous low-k films deposited without and with AM.

4. Conclusions
We have proposed a novel one-step method for synthesizing nano-particle composite porous low-k films. The following conclusions are obtained in this study:
1. Size of nano-particles is controlled in a size range of 1-20 nm by the duration of pulse rf discharge.
2. Rapid transport of nano-particles at a velocity more than 60 cm/s is realized by pulse rf discharges with AM. Two important parameters for the rapid transport are the discharge voltage and the period of AM.
3. The deposition rate with AM is 0.65 nm/s, which is 7 times as high as that without AM, while dielectric constant k =1.1-1.4 and porosity =60-63% of the films with AM are nearly equal to those without AM. Therefore deposition of porous low-k films using pulse rf discharges with AM is a promising method for increasing the deposition rate without varying the properties of films.

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