Numerical modeling of controlled deposition of silicon nanoparticles using a pulsed RF argon-silane plasma

C. Larriba-Andaluz and S.L. Girshick

Department of Mechanical Engineering, University of Minnesota, US-55455 Minneapolis, MN, U.S.A.

Abstract: Numerical simulations were conducted using a 1D model of a pulsed RF argon-silane plasma in which silicon nanoparticles nucleate and grow. We show that by controlling pulse frequency and duty cycle, and by applying a DC bias to the film growth substrate during the afterglow phase of each cycle, one can control the fluxes of silicon nanoparticles to the substrate, as well as the nanoparticle size and impact energy.

Keywords: dusty plasmas, pulsed plasmas, silicon nanoparticles, numerical modeling

1. Introduction

Recently it was hypothesized that epitaxial growth of silicon films at relatively low substrate temperatures (<200 °C) could be achieved by energetic impact of very small silicon nanoparticles on c-(100) Si substrates, under conditions where the nanoparticle impact velocity is high enough to cause particle melting or amorphization, but not so high as to cause film damage [1]. A possible way to achieve this is to pulse an RF silane-containing plasma, under conditions where silicon nanoparticles nucleate during the ON phase of each pulse, and then to apply a positive DC bias to the film substrate during the afterglow of each pulse. During the ON phase, nanoparticles nucleate, grow, and become mostly negatively charged, causing them to be trapped in the plasma. During the afterglow they are accelerated to the substrate by the applied bias. By controlling pulse frequency, duty cycle and bias voltage, one could potentially control the fluence, size and impact energy (eV/atom) of the collected nanoparticles.

To investigate this scenario we utilized a previously developed 1D numerical model [2], modified to consider plasma pulsing and applied substrate bias. This model self-consistently solves for the coupled behavior of the plasma, chemistry, and aerosol. Briefly, the plasma model includes electron and ion population balance equations, the electron energy equation under the assumption of a Maxwellian energy distribution, and Poisson’s equation for the electric field. The chemistry module considers silicon hydride neutral and ionic species containing up to two Si atoms. The rate of formation of anions containing three Si atoms is taken as a surrogate for the particle nucleation rate. An aerosol sectional model is used to model the evolution of the particle size and charge distributions [3]. Phenomena considered include particle surface growth by chemical vapor deposition, size- and charge-dependent coagulation (accounting for the effect of image potentials for interactions between charged and neutral nanoparticles), charging by electron and ion attachment, based on Orbital Motion Limited theory [4], and nanoparticle transport by electric force, neutral drag, ion drag and Brownian diffusion.

Practical implementations of the proposed method for growing epitaxial silicon films will likely involve silane-hydrogen plasmas. For the simulations presented here, the conditions are the same as for the simulations in Refs.2-3, involving a silane-argon plasma, except that the plasma is pulsed and a DC bias is applied to the lower electrode during the afterglow phase of each cycle. The conditions include 13.56 MHz RF frequency, 100 V applied RF voltage, 100 mTorr pressure, 4-cm electrode gap, 300 K gas temperature, and a 30:1 ratio of argon to silane that enters through the upper electrode with a velocity of 27 cm/s. The RF pulse frequency is set to 50 Hz, with a duty cycle of 50% and a positive DC bias on the lower electrode of 100 V that is applied only during the afterglow phase of each cycle.

2. Results

Fig. 1 shows contour plots of the predicted nanoparticle size distribution vs. the axial position across the electrode gap, at three specific times during a single pulse cycle: (a) when the plasma is on, 6 ms into the 10-ms ON pulse; (b) 0.4 ms after the applied RF voltage is turned off; and (c) 3 ms after the applied RF voltage is turned off, by which time almost all charged nanoparticles and ions have been collected. The color scheme in the figure represents the particle size distribution function, while the white contour lines represent the average net particle charge for a given size and location. While the plasma is powered, nanoparticles nucleate and grow (a). Immediately after the applied RF voltage is turned off a positive DC bias voltage is applied to the lower electrode (axial position zero), accelerating the negatively charged nanoparticles towards that electrode (b). If sufficient afterglow time is provided, all of the negatively charged nanoparticles are collected, and only very small neutral particles remain, which freely diffuse towards both electrodes (c). Note that these results are for the fourth pulse cycle, i.e., the cycle begins 60 ms following plasma initiation. The results for the first few cycles differ from each other,
representing a startup transient. By the cycle shown, however, the system has reached a periodic steady state, with the results for subsequent cycles repeating without any evident change. Once particles grow beyond a certain size, virtually 100% of them are negatively charged, and these particles are all collected by the biased substrate during the afterglow phase. The remaining population of nanoparticles left behind is quite small, and repeats its size and spatial distribution from cycle to cycle.

Fig. 2 shows density profiles of all charge carriers, including electrons, positive ions (summed together, with $\text{Ar}^{+}$ dominating), negative ions (summed together, with $\text{SiH}_2^-$ and $\text{SiH}_3^-$ dominating), total charge carried by negatively charged nanoparticles, and total charge carried by positively charged nanoparticles, at the same three times as in Fig. 1. Fig. 2a shows that when the applied RF voltage is on, negatively charged species, including electrons, anions and nanoparticles, are focused in the center of the plasma by the electric field, leaving a positive space charge in the sheaths. The positive ion density also peaks in the center, and exceeds the electron density, maintaining quasineutrality. When the applied RF voltage is turned off, free electrons are lost from the system within a few microseconds due to their high mobility, and thus do not appear in Fig. 2b, which shows density profiles 0.4 ms into the afterglow. One sees here that anions and negative nanoparticles are pulled towards the bottom electrode by the applied DC bias. Interestingly, the cations and positive nanoparticles are not only pushed towards the upper electrode by the positive bias on the lower electrode, but are also transported towards the lower electrode, pulled, in effect, by the anions and negative nanoparticles, again maintaining quasineutrality. Thus the negative and positive nanoparticle populations are both pulled toward the bottom electrode, displaying a type of ambipolar diffusion. Finally, when all negative charge carriers have been collected, some positive ions and nanoparticles remain, as seen in Fig. 2c. These are now pushed to the upper electrode by the biased substrate, although it is difficult to see the slope in their profiles on the logarithmic scale of the plot.

The volume fluxes of negative, neutral and positive nanoparticles to the lower electrode are shown in Fig. 3, for three different pulse cycles beginning with the third cycle, i.e., beginning at 40 ms following plasma initiation. During the RF ON phase of each cycle, only positive and neutral nanoparticles reach the electrode, while negative nanoparticles are confined in the center of the plasma.
Immediately after the RF voltage is turned off and the DC bias is turned on, negative nanoparticles are quickly collected by the bottom electrode, while positive particles are repelled. The negative particles are effectively all collected by the biased electrode within about 2 ms. For the neutral nanoparticles, which are not directly affected by the electric field, the flux is relatively constant. During the rest of the afterglow phase, only neutral particles reach the electrode, although this diffusion process is slow relative to the time scale of the pulses, as only a small decay in the neutral flux is observed before the next pulse begins.

From the viewpoint of the potential application, creation of epitaxial Si films by energetic impact of small nanoparticles, deposition of neutral nanoparticles, which are not accelerated, is undesirable. However, while neutral nanoparticle deposition cannot be completely avoided, the simulation results indicate that it accounts for less than 0.1% of the total volume (equivalently, mass) flux of nanoparticles to the substrate. That is the result of two factors. First, flux equals the product of density times velocity, so the flux of neutral nanoparticles is relatively low in spite of their fairly high density. Second, the neutral nanoparticles are, on average, smaller than the negatively charged nanoparticles – 1.0 nm for the neutrals versus 2.7 nm for the negative nanoparticles, as shown in Fig. 3. That is primarily because as nanoparticles grow they become much more likely to be negatively charged. Thus, low-velocity deposition of relatively large nanoparticles, which would lead to defects and thus be undesirable, is quite unlikely. It is also interesting to note that positively charged nanoparticles are collected during the cycle ON phase, and these are accelerated to the substrate by the sheath potential. However the densities of positive nanoparticles are quite low, and thus so are their fluxes.

In conclusion, our preliminary simulations indicate that pulsing of the RF voltage together with application of a positive DC bias to the film substrate during the plasma afterglow phase is a promising method for producing and controlling energetic fluxes of very small nanoparticles to a substrate, which has been hypothesized to facilitate growth of epitaxial silicon films. Simulations that will be reported elsewhere also investigated effects of pulse frequency, duty cycle and bias voltage, and show that these parameters can be adjusted to control the size and fluence of nanoparticles to the substrate. Further simulations will turn to the silane-hydrogen system that is a likely candidate for growth of high-quality epitaxial silicon.

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4. References