ECR-PECVD FOR THIN FILM DEPOSITION

High density plasma chemical vapor deposition (HDP-PECVD) technology was invented in late seventies and is in broad use in industry since the beginning of nineties. Interestingly enough, the term “high density plasma” is not clearly defined. In microelectronic industry, as well as in low-pressure (technological) plasma community, the accepted definition will probably be “plasma sustained in high density plasma system” as de facto only inductively-coupled plasma (ICP, alternatively also called transformer-coupled plasma, or TCP), electron cyclotron resonance (ECR) or Helicon systems will be eligible to be called “high density plasma system”. Those systems operate at different frequencies, microwave 2.45 GHz for ECR and various radio frequencies (RF), which typically range from 2 MHz to 50 MHz for ICP or Helicon systems. They all usually have separate RF biasing of the substrate holder in order to control the ion bombardment energy, while main power supply provides bulk plasma ionization and dissociation. Even if such systems frequently operate at the power levels that create plasma densities below maximal, which can reach several $10^{12}$ cm$^{-3}$ in the source region, our point of view that term “high density plasma” shall still be used in such case. What is common for those systems and set them apart from the rest is the operation pressure, which is significantly lower than for traditional 13.56 MHz RF capacitively-coupled (CCP-PECVD), even though, ICP systems are capable to operate at very high pressures. It is the operation pressure that will lead to different electron energy distribution function (EEDF) for example and strongly affect the nature of products of dissociation, in our case – precursors for the deposition. It is the pressure that determines the specifics of HDP-PECVD, such as deposition process mechanisms and properties of the films. The precursors for deposition traveling from the point of creation to the surface of the substrate may (and will) undergo collisions, number of which will depend on the pressure in a reactor, and lower the pressure in the system, more it will lead to the primary dissociation products to arrive at the surface in initial state. Of course, low pressure operation also lead to efficient energy transfer to electrons, as number of elastic collisions decreases, thus providing fuller dissociation and ionization of precursors. At the end of the day, any new technology initially appears to answer the needs of industry that cannot be answered by existing techniques and after starts its own life, extending sometimes into new areas and/or ceding its positions. High density plasma PECVD is not an exception. Beyond its main use in microelectronics, even if occasionally, it has found applications, for instance in the deposition of optical coatings, such as antireflection
coatings (ARC), Bragg reflectors and graded index (so-called “rugate”) filters, in photovoltaics research, in surface treatment, etc.

ECR systems, as one of the direction, which the development of deposition technology took, is based on the effect of resonance power coupling, that takes place

Figure 1: Principle of ECR power coupling.

When plasma is subjected to an alternating electric field \( E \) in the presence of a perpendicular static magnetic field \( B \), the electrons will receive energy from the electric field but will gyrate because of magnetic field. Consider the arrangement shown in Fig. 1 (magnetic field is normal to the page). Let us assume that an electron is accelerated to the left by the time-varying electric field. If the frequency of the alternating electric field \( \omega \) is equal to the cyclotron frequency of the electron \( \omega_{ce} \), the magnetic field will turn the electron around just in time again to be accelerated in the opposite direction by the time electric field changes polarity. Thus, the electron gains energy as \( E \) oscillates in both directions (provided there are many oscillations between collisions), and a resonant condition is created. The frequency given by the equation 1 provides us with numerical value of the electron cyclotron frequency in a given magnetic field with strength \( B \).

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\omega_{ce} = \frac{e \cdot B}{m_e} \tag{1}
\]

Good microwave energy coupling is directly related to synchronization between the combined electron-neutral and electron-ion collision processes and the excitation frequency \( \omega \). For different gases the optimum pressure range for efficient discharge breakdown and maintenance with 2.45 GHz microwave energy usually occurs between 0.5 and 10 Torr.
However, when static magnetic field with strength of 875 Gauss is impressed on the energy coupling process, the electron cyclotron resonance effect leads to very efficient energy transfer from the electric field directly to the electrons. For high pressures, very little resonance is seen as electron collisions occur so frequently that the electron cannot be turned by the magnetic field in time to catch the reversing electric field. Under these conditions the process of heating of the electrons is purely collisional. At low pressures, however, there is strong resonance, and ECR heating is taking place. For helium, for example, transition between the two heating regimes occurs between 3 and 0.5 Torrs.

A steady state microwave discharge is characterized by equality between the electromagnetic power absorbed by the plasma and power losses in the plasma volume. The absorption process includes the microwave energy absorption by both the electron and ion gases. Owing to the fact that work done on a charged particle by an electric field between collisions varies inversely as the particle mass, the energy gained by the electron is much greater than the energy gained by the ion. Therefore, direct energy transfer to the plasma takes place through Joule (elastic and inelastic heating) and electron cyclotron heating of the electron gas.

Because at a certain plasma density, called the critical density $n_c$, an electromagnetic wave of frequency lower than $\omega$ is reflected from the plasma boundary, it is usually assumed that plasma electron and ion densities within the microwave discharge are limited to less than the critical density, given by

$$n_c = \frac{m_e \cdot \varepsilon_0 \cdot \omega^2}{e^2}$$

Or $n_c = 1.24 \cdot 10^{-2} \cdot f^2$, where $f$ is the excitation frequency. This implies that, with 2.45 GHz excitation, plasma densities are limited to a maximum of $7.4 \cdot 10^{10}$ cm$^{-3}$. In practice, waveguide applicators produce slightly higher densities, and cavity applicators are capable of producing densities of 10 to 50 times the critical densities at low pressures, and densities above 100 times the critical densities at high pressures. The ability to produce high densities is due to evanescent wave penetration into the plasma. This type of coupling is greatly enhanced in cavity applicators because of their ability to impress a high standing-wave electric field against the discharge without reflecting power from applicator.

Typically, due to finite wavelength, both systems, waveguide-based and cavity-based, have natural limitations in terms of uniformity on large areas. Special type of applicators, multidipolar antennas, developed by Dr. Jacques Pelletier (from the Laboratory of Subatomic Physics and Cosmology in Grenoble, France), allows to bypass this limitation. Arranged in
matrix of alternative polarities such applicators allows to create uniform dense plasma on large areas. In our laboratory we have two MDECR reactors, dedicated to the thin film silicon and thin film dielectrics deposition, respectively.

Figure 2: Mounted on DN250 ISO-K flange MDECR plasma source equipped with 7 MDECR antenna applicators. This source is used for a-Si:H and μc-Si silicon deposition
Figure 3: HDP-PECVD system equipped with MDECR 16 MDECR antenna applicators plasma source and in-situ spectroscopic ellipsometer UVISEL used for low-temperature deposition of dielectrics (SiNx, SiO2 and oxynitrides).

Figure 5: TEM photograph of the MDECR-deposited SiO2 layer on silicon.
Figure 6: Evolution of FTIR spectra of SiO$_x$N$_y$ with O$_2$/O$_2$+N$_2$ gas flow ratio.
Figure 7: Optical filter grown by MDECR-PECVD and its transmission characteristics.

A.1 The effect of temperature of the substrate:

The deposition rate with the substrate temperature is found to be constant or to decrease in the range of temperatures 50 °C and 500 °C. The substrate in those experiments was electrically grounded and heated to specified temperature. This indicates that the temperature is not affecting the rate of SiH₄ decomposition but rather influence the residence time of the silane on the substrate surface. The effects of heating of the sample may be an increase of the oxide density (lower etch rate) through more efficient removal of the water, which is the reaction product. A substrate temperature under 400°C may not cause SiH₄ dissociation and thus does not contribute positively to the deposition rate. The evolution of the growth rate is the same also when the substrate is biased. As the wafer temperature increases, the rate of neutrals desorption increases, slowing down the deposition. Thus, in the reasonable temperature range, heating can only be considered as a way to increase the quality of the layer and not to increase the deposition rate.

A.2 The influence of microwave power.

The deposition rate is increasing linearly with the microwave power supplied to the plasma for some experiments, while it stays constant in others. Obviously, the reason for such
discrepancy is in the proportion of silane molecules being dissociated and in injection system (way of delivery of silane to the substrate) implemented in specific machine. This proportion is certainly increased with the power to certain value (around 100 %, since SiH4 is very easily dissociated molecule), usually at relatively low microwave power and, consequently, the number of reactive species is increasing at first, but then stay constant. Ion current on the surface of the substrate increases too with power, whereas sheath voltage, hence the energy of the ions striking the surface, exhibits more complex behavior.

A.3 The influence of process pressure.

Growth rate is usually increasing with pressure, but only if the gas flows are scaled correspondingly. Some discrepancy in experimental results is most probably due to injection-specific effects, not because of the change in reaction mechanisms, since for low pressure PECVD, such as in ECR-PECVD (10^-4-10^-3 Torr), reaction is always takes place on the surface and virtually never in the volume. Collision rate between neutrals is low and consequently probability of volume reaction is low too. We can explain the saturation or decrease of ion current by the drop in the ionization efficiency, due to higher collision rate between electrons and neutrals in the plasma and decrease of mean free path for neutrals.

A.4 The influence of RF bias

The ECR plasma has usually very low plasma potential (several volts) in comparison with RF plasma. When we need energetic ion bombardment of the growing film, we have to apply RF bias on the substrate holder. It involves a separate, usually 13.56 MHz power supply and a matching network (automatic or manual). In this way energy of the ions striking the surface may be controlled independently and varied from tens to hundreds of electron volts. Usual tendency is that, the growth rate of the silica film decreases with the increasing bias voltage (-20 V to −100 V). Ion bombardment induces some physical sputtering (depending on bias voltage) and, therefore, decreases the deposition rate. However, with substrate bias between 50 V and 250 V, both index of refraction and growth rate of a silicon oxynitrides were found to increase simultaneously. The increase of refractive index is due to densification, resulting from an increase of ion bombardment. Increase of deposition rate, which is more difficult to explain, however, may be due to the contribution to the growth dissociated under ion bombardment, otherwise, non-reacting neutral silane molecules. Despite the high dissociation rate in the ECR plasma, neutral molecules constitute the majority of the species arriving at the surface. Ion bombardment here can significantly alter surface reactions.

A5. Oxygene /silane flow ratio:

In practice, the gas flow ratio R=O2/SiH4 (sometimes R=SiH4/(SiH4+O2) is used) provides the most direct control of the film stoichiometry, while SiH4 flow control the deposition rate. From the chemical reaction SiH4 + 2 O2= SiO2 + 2 H2O one can deduce minimal ratio of oxygen to silane flows R = 2 to obtain stoichiometric SiO2. In the reality however, such ratio shall hold true at the growth surface. Since it is not easy, if possible at all, to probe the quantities of species arriving onto the surface, and given unknown dependence of residence time of the species at the surface on temperature, such flow ratio may only be deduced experimentally. Given differences of the injection systems designs one shall treat with care published data on the optimal gas flow ratios for SiO2 deposition. However general trends should hold for all systems. For a constant total gas flow of oxygen and silane, the
deposition rate of silica will have a maximum for a certain value of the ratio. For higher ratios the deposition rate would drop owing to depletion of the gas phase with silane. For lower ratios the rate will drop too, while the index of refraction will increase strongly due to deposition of silicon-rich SiOx. For the deposition of a high quality of silica, the deposition rate is, generally, found to be limited by the total silane flow at any given oxygen-to-silane flow ratio. The deposition rate increases linearly with the silane flow into the reactor.

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