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Processing of electronic materials by microwave plasma

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Abstract: It is now generally accepted that the frequency $\omega/2\pi$ at which a high frequency (HF) discharge is excited has considerable influence on the properties of the plasma. The analysis which has been developed to account for observed differences between microwave (MW) and radiofrequency (RF) discharges, both used extensively in electronic materials processing, calls on the dependence of the electron energy distribution function (EEDF) upon ω.

This review of MW plasma processing is divided into four parts: following a brief introduction, the second section outlines kinetic modeling of low-pressure HF discharges; the approach used allows us to calculate certain key parameters which can be compared with experimental data.

In the third section, we review the current state of available MW plasma technology for integrated circuit (IC) fabrication, including electron cyclotron resonance (ECR) systems.

The fourth and final section reviews published work on electronic materials processing operations with MW plasmas, namely dry etching, stripping of photoresists, and plasma-enhanced chemical vapour deposition (PECVD) of thin films.

1. Introduction

The processing of electronic materials has been the principal industrial use of low-pressure plasma chemistry since the late 1960's (1,2). This involves a) "dry-etching" of silicon, its compounds, compound semiconductors, metals, polymers, etc., on sub-μm scales required by current VLSI and ULSI technologies, and "stripping" of organic photoresists (1-3); and b) deposition of thin film materials (1,2,4).

The plasmas for these processes use almost exclusively a source of high frequency (HF) electrical excitation, either in the radiofrequency (RF) or microwave (MW, ≥300 MHz) regime; the particular choice of excitation frequency, however, is usually restricted to ITU-approved ISM bands[a], for example 13.56 MHz (RF) and 2.45 GHz (MW).

Microwave-excited plasmas have always enjoyed a distinct place in the literature. McTaggart (5), in his monograph on plasma chemistry up to 1964, wrote extensively about MW plasmas. Wightman (6), in a review article entitled "Chemical Effects of Microwave Discharges" which surveyed the literature from 1965 to 1973, made the statement that "there is sufficient evidence to indicate that chemical results obtained with the microwave plasma differ significantly from other plasmas". Two further review papers on the subject, by Lebedev and Polak (7), and by Musil (8), followed in 1979 and 1986, respectively; and finally, in 1992, two books edited by Moisan and Pelletier (9), and by Ferreira and Moisan (10).

Several authors have indirectly addressed the "distinctness" of MW plasmas, by writing about frequency effects in plasma processing, namely Flamm (11), Lebedev and Polak (7), Wertheimer and

Note a: ITU: International Telecommunication Union; ISM: Industrial, Scientific and Medical.

Moisan (12), and Moisan et al. (13,14). Clearly, then, investigations on the subjects of plasma excitation frequency effects and of processing in ultra-high frequency discharges are now quite extensive.

A third category of plasma process, besides the etching and deposition reactions mentioned above, has recently gained prominence in sectors of the economy other than microelectronics: plasma-induced surface modification of materials (mostly polymers), for example for enhanced bonding, is increasingly important in automotive, aerospace, and packaging industries, to name only a few examples; a critical review (15) is shortly to appear in the first of two issues of J. Adhesion Science and Technology, which are devoted entirely to this subject. Here, too, MW plasmas play a prominent role.

The purpose of the present paper is to discuss primarily the first two types of microwave plasma processes mentioned above, etching and deposition, specifically their application to the processing of electronic materials.[b] In section 2 we outline the kinetic modeling of low-pressure MW discharges following which, in section 3, we review the evolution of apparatus for MW plasma processing. A subsection is devoted to electron cyclotron resonance (ECR), a subject which has received much attention in recent years. Finally, in section 4, we review MW plasma processing of electronic materials, first etching and stripping, then deposition of thin films.

2. Theory

At the reduced pressures (10^{-3} Torr $\lesssim p < 10$ Torr) used for MW plasma processing of electronic materials, the average energy of the electrons is much higher than that of ions and neutral species. The excitation and ionization of atoms and molecules are thus essentially provided by electron impact on these heavy species. This implies that the shape of the electron energy distribution function (EEDF), $F_0(u)$, plays a major role in the density distribution of the various excited states of atoms and molecules, and in determining the ion density n_i for a given power density P_A deposited in the plasma (13). This is outlined succinctly in the following subsections.

2.1. Power Transfer to the Plasma

2.1.1. Power absorbed from the field per electron, θ_A — In MW discharges, the operating frequency f = $\omega/2\pi$ is sufficiently high that the massive ions do not respond to the time-varying EM field; only the electrons are able to absorb energy from the field. In a DC discharge, an electron is accelerated continuously by the applied electric field **E** until it collides with another plasma constituent. The situation is totally different in high frequency (HF) discharges (which include both RF and MW cases): an electron is accelerated by the force $\mathbf{F} = -e\mathbf{E}$ ($-e$ is the electronic charge) in one direction during the first half of the period, and in the opposite direction during the second half. Averaged over one period, no net work is done and no energy is gained by the electron. It is only when this harmonic motion is interrupted by a collision that there is a net transfer of energy to the electron, which corresponds to the energy absorbed over the uncompleted period.

To characterize this power transfer, it is now customary to introduce the parameter θ_A, the power absorbed from the field per electron. Consider the plasma as being composed of a single fluid, the electrons (ions and neutral species being at rest), and neglect for simplicity the electrons' thermal motion (cold plasma approximation). The equation of motion is then

$$m_e \frac{d\mathrm{v}}{dt} = -e\mathbf{E} - m_e \nu_c \mathrm{v} \tag{1}$$

where m_e is the electron mass and ν_c is the average (effective) electron-neutral collision frequency for momentum transfer. Since we assume a cold plasma, the electron velocity is fully governed by the electric field $\mathbf{E} = \mathbf{E}_0 \exp(i\omega t)$; thus, from (1),

$$\mathrm{v} = \frac{-e\mathbf{E}}{m_e(i\omega + \nu_c)}. \tag{2}$$

Note b: Chapters by J. Paraszczak and J. Heidenreich (16,17) in references 9 and 10 also specifically deal with electronic materials processing with MW plasmas.

Since the work done by the electron per unit time is F•v, we obtain, from its average over one HF period,

$$\theta_A = \overline{-e\mathbf{E}\cdot\mathbf{v}(t)} = \frac{e}{2}\mathrm{Re}(\mathbf{E}\cdot\mathbf{v}) = \frac{e^2}{m_e}\frac{\nu_c}{\nu_c^2+\omega^2}\overline{E^2} \tag{3}$$

where Re means "the real part of", and the mean square value $\overline{E^2}=E_0^2/2$. We confirm that $\theta_A=0$ when $\nu_c=0$.

2.1.2. Power lost per electron to the plasma, θ_L, and power balance — Electrons transfer the energy acquired from the field to the plasma through collisions with heavy particles. The power lost on the average per electron in such collisions is given by (18)

$$\theta_L = \frac{2m_e}{M} <\nu_m(u)u> + \sum_j <\nu_j(u)>eV_j + <\nu_i(u)>eV_i, \tag{4}$$

where M is the atom (molecule) mass, ν_m is the electron-neutral collision frequency for momentum transfer for an electron of microscopic energy u, and ν_j and ν_i are the electron collision frequencies leading to excited atomic (molecular) species "j", and to ionization, respectively; eV_j and eV_i, respectively, are the corresponding energy thresholds for excitation and ionization. The bracket < > means the average value over the EEDF.

Charged particles can "leave" the plasma by ion-electron recombination, either in the plasma bulk (volume recombination), or as a result of diffusion to the discharge vessel wall. When the electron density is not too high (typically $n \le 10^{12}$ cm^{-3}) and the average energy is not too small ($<u> \ge 1$eV), one can assume that the charged particles are lost by diffusion to the wall (19). In this case, provided that atoms (molecules) are excited and ionized by single electron impact events from the ground state, <u> (or the electron temperature T_e, if the EEDF is Maxwellian) and θ_L can be assumed, as a first order approximation, to depend only on the *discharge conditions* (discharge vessel dimensions and shape, nature and pressure of the gas, frequency, and static magnetic field intensity), whatever the microwave power density absorbed in the discharge.

Under steady-state conditions, the power absorbed from the field adjusts to compensate for the loss of electron energy to the plasma, yielding the power balance equation

$$\theta_A=\theta_L, \tag{5}$$

the common value being the parameter θ. Expression (4) shows that this parameter depends on the shape and average energy of the EEDF. Therefore, the determination of the EEDF is important, the subject we discuss next.

2.2. Influence of ω on the Plasma Characteristics.

2.2.1. Dependence of the EEDF on ω — The EEDF, $F_0(u)$, is obtained by solving the Boltzmann equation from the kinetic theory. This equation describes the behaviour of electrons submitted to the action of electric and magnetic fields, in the presence of collisions. At MW frequencies the EEDF is stationary, meaning that it cannot follow the oscillation of the EM field with time. In the absence of a static magnetic field, one can then write the stationary and spatially homogeneous Boltzmann equation as

$$-\frac{2}{3}\frac{d}{du}[u^{3/2}\nu_m(u)u_c(u)]\frac{dF_0}{du}=S_o(F_0) \tag{6}$$

where the term $S_0(F_0)$ describes the collisions of electrons among themselves, and with the other constituents of the discharge; the quantity

$$\nu_m u_c = \frac{e^2}{m_e}\frac{\nu_m(u)}{\nu_m^2(u)+\omega^2}\overline{E^2} \tag{7}$$

has units of energy per second, and it represents the average power transferred from the electric field to electrons of energy u. This transfer is a function of u and ω, and it is maximum for $\nu_m(u) = \omega$. Thus, as the field frequency $\omega/2\pi$ sustaining the discharge is varied, the maximum power transfer shifts towards different values of u, which affects the shape of the EEDF. This is the origin of the frequency effect in HF discharges. At a fixed value of ω, the dependence $\nu_m(u)$ is a property of the particular gas under consideration.

2.2.2. Three limiting cases for the influence of ω *on* $F_0(u)$ — Three limiting cases can provide us with an overall picture of the influence of ω on the EEDF (13). Consider, first, the influence of the ratio ν_m/ω when electron-electron collisions are negligible (which is typical for an ionization degree $n/N < 10^{-4}$, n and N being the densities of electrons and molecules, respectively). Two limiting cases are then in order: $\nu_m/\omega = 0$, the so-called microwave case, and $\nu_m/\omega \to \infty$, which corresponds to a DC discharge (or an RF discharge, but not so low in frequency that F_0 is non-stationary). The third limiting case is that of dominating electron-electron collisions, and it corresponds to a Maxwellian EEDF. These three EEDFs differ significantly among themselves. To characterize these differences, we distinguish between the electrons in the bulk of the EEDF and those with energies exceeding the threshold energy eV_1 for the first excited level of the atom (molecule). The part of the tail between eV_1 and eV_i, the threshold energy for ionization, is most densely populated in a DC discharge; the corresponding populations in the microwave case and in the Maxwellian EEDF are much lower, and close to each other (13). This translates into a higher average electron energy in a DC discharge; when the electron-electron collisions are taken into account simultaneously with the electron-neutral collisions, the EEDF differences between the DC and microwave cases diminish as n/N increases; the differences completely disappear when the degree of ionization is sufficiently large. From this, we conclude that to observe a frequency effect in HF discharges, the value of n/N must not be too large, typically below 10^{-4} in most gases.

2.2.3. Influence of ω *on the parameter* θ — We have indicated above (section 2.1.2.) that if the charged particles are lost by diffusion to the wall, and if excitation and ionization occur by single electron impact events, the values of θ and $\langle u \rangle$ depend only on the discharge conditions. One can show that in Ar (and in many other gases) θ decreases with increasing ω, and it has its lowest value in the Maxwellian case, provided $p_0R \geq 0.1$ torr-cm (R being the discharge vessel radius and p_o the gas pressure at 0°C). As a result, for a given HF power density absorbed in the plasma, P_A, which is related to θ by

$$P_A = n\theta, \tag{8}$$

n increases with ω and attains its highest value for a Maxwellian EEDF *(provided p_0R is large enough).* We conclude that for a given P_A value, MW plasmas are generally a more "efficient" source of ions than RF discharges, unless n in the latter is high enough for the EEDF to be Maxwellian.

2.2.4. Influence of ω *on* $\dot{n}_j$ — Consider, for simplicity, the frequent case where excited and ionized species are created by single electron impact events on the atoms (molecules) in the ground state. The density of species created in the excited state "j" per second is then

$$\dot{n}_j = \langle \nu_j \rangle n \equiv C_j N n \quad ; \tag{9}$$

the rate of excitation C_j is given by

$$C_j = (2/m_e) \int_{V_j}^{\infty} Q_j(u) F_0(u) u \, du \tag{10}$$

Q_j being the cross-section for electron impact which characterizes this particular process. Two cases must now be considered:

(i) **Constant n condition.** Here, only the variation of C_j with ω affects the value of $\dot{n}_j$; in argon (13), for $eV_j \leq eV_i$, C_j is largest in a DC discharge, among the three limiting cases of section 2.2.2. From equation (9), assuming constant n, $\dot{n}_j$ is therefore largest in a DC discharge.

(ii) **Constant P_A condition.** In practice, one is more interested to know which of the three limiting cases leads to the highest $\dot{n}_j$ value for a given P_A, since this governs the process efficiency. Such a calculation has been done with argon as the carrier gas, the rate of creation of chemically reactive species ($\dot{n}_j$) deriving from a small addition of reagent gas which is assumed not to modify the carrier gas properties.

Now, equation (8) indicates that n varies with ω, since θ is a function of ω; the values of θ required for the calculation, in turn, are those of the carrier gas (argon), and these values are available from reference (20). The results may be summarized as follows: for a given P_A, the DC case ($\nu_c/\omega = \infty$) yields the lowest $\dot{n}_j$, while the highest $\dot{n}_j$ value usually occurs when the EEDF is Maxwellian; for more details, the reader may consult reference (13).

Clearly, a comparison of RF and MW discharges, from the point of view of process optimization, calls for constant n or constant P_A conditions. Although the results presented above pertain to the case of dilute reagent in argon, they nevertheless appear to extend to other gases, at least qualitatively (21).

2.3. The Role of a Static Magnetic Field in HF Discharges

For certain plasma processes, for example anisotropic etching (see section 4.1.), it may be advantageous to operate at very low pressures where a high ratio of ions to reactive neutrals can be achieved. In section 2.1.1., we showed that a certain minimum number of electron collisions is required to sustain an HF discharge; the presence of a static magnetic field B_0 lowers this minimum threshold. The action of B_0 on an HF discharge can be separated into two distinct effects.

2.3.1. Wall losses of charged particles — The charged particles in a magetoplasma undergo helicoidal motion around the B_0 field lines, on account of the Lorentz force; considering the case of a cylindrical discharge vessel with an axial field B_0, the higher the value of B_0, the lower will be the radial diffusion rate of charged particles to the wall. The motion of charged particles in a plane perpendicular to B_0 is circular and periodic, and for electrons the frequency is the so-called electron cyclotron frequency $f_{ce} = \omega_{ce}/2\pi$, where $\omega_{ce} = eB_0/m_e$. The electrons are effectively confined only when there are many cyclotron gyrations between successive collisions, that is, when $\nu_c \ll \omega_{ce}$. The value of θ_L (hence also θ_A) decreases with rising B_0 value, as shown in Fig. 1. The minimum gas pressure p_m for which an HF discharge can be sustained is determined by the maximum θ_A value that can be achieved; a lowering of θ with rising B_0 makes this θ_A value appear at lower p_m than for the case when B_0=0.

2.3.2. Resonant power transfer at $\omega = \omega_{ce}$ — When the angular frequency of the HF field equals ω_{ce}, the so-called electron cyclotron resonance (ECR) condition is fulfilled. ECR requires that an electromagnetic wave propagate in the discharge with an E-field component in the plane perpendicular to B_0, and which rotates around the B_0 lines in the same direction as the electrons in their cyclotron motion. When, for a given value of ω, the value of B_0 is adjusted such that $\omega_{ce} \equiv \omega$ (B_0 = 0.0875 T for $\omega/2\pi$ = 2.45 GHz), the electrons "see" a constant E-field in their own frame of reference, and this field accelerates them in a continuous mode. Of course, this energy is then transferred to the heavy particles by collisions. Contrary to the B_0 = 0 case described in section 2.1.1., where a low value of ν_c inhibits power transfer, this is not the case for resonant transfer. Figure 1 shows that no anomaly or discontinuity in θ occurs near $\omega_{ce}/\omega = 1$, as expected from the fact that θ_L is governed by charged particle diffusion to the wall.

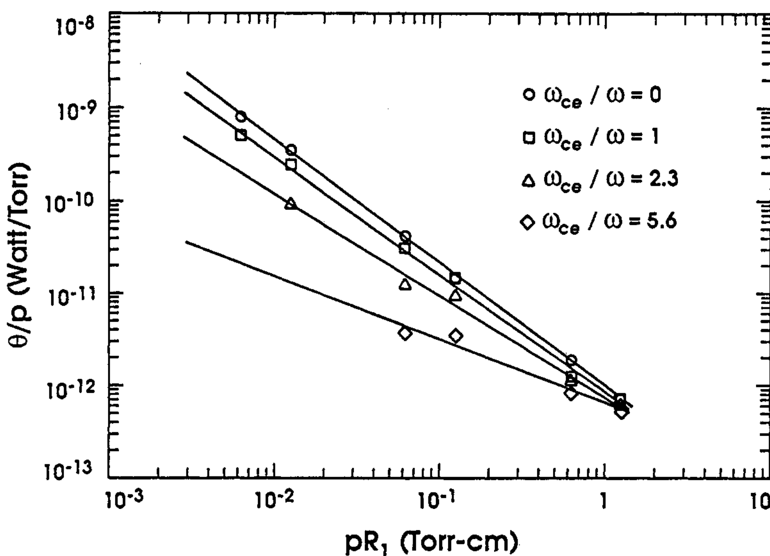

Figure 1. Measured values of θ/p versus pR_1 (see text for definition of symbols) for a surface wave magnetoplasma in argon, with different B_0 field values ($\omega/2\pi$ = 600 MHz, R_1 = 13 mm). (From ref. 9)

3. MW Plasma Reactor Design

3.1 General Considerations

Until recently, most integrated circuit (IC) fabrication operations have been carried out using RF reactors, either of parallel plate or of "hexode" designs, the electrodes being in direct contact with the plasma (1-3,22,23). In such reactors, which permit several (up to 24) wafers to be processed simultaneously, the applied RF power P_{RF} determines not only $\dot{n}_j$, the creation rate of chemically reactive precursors (mostly neutral species), but also ϕ_i, the flux of energetic ions normal to the wafer surface. The mean ion energy $\langle E_i \rangle$ is important in both etching and deposition operations, as will be shown later. The value of $\langle E_i \rangle$ is governed by the potential drop across the plasma sheath, and it can readily attain tens or hundreds of eV (24). In the case of most MW discharges there are no internal electrodes, the sheath potentials are low ($\lesssim$ 20V), and ion bombardment effects are negligible, unless one deliberately chooses to create an elevated negative substrate bias potential V_s. This can readily be achieved with a separate (RF) power supply, and it has the important advantage of decoupling the values of $\dot{n}_j$ and ϕ_i (25,26) (see also section 4).

In the following, we list several ways of classifying MW discharges:

(i) "Proximity": the part being processed may either be in direct contact with the plasma, or it may be located remotely (or "downstream") where only long-lived species (largely neutrals) in the plasma effluent contribute to the process chemistry; both of these situations have practical importance in IC fabrication, as will be shown in section 4.

(ii) Gas pressure, p: diverse IC fabrication operations may call for pressures ranging from very low values ($p \lesssim 1$ mTorr, or 0.13 Pa) to "high" values (several Torr, > 10^2 Pa); stable MW plasmas at $p \lesssim 10$ mTorr (1.3 Pa) generally require the presence of a static magnetic field B_o, for example under ECR conditions (see section 2.3.2.). Having achieved particular technological importance in IC fabrication over the past fifteen years, the special case of ECR reactors is discussed separately in section 3.2.

(iii) Plasma geometry: Depending on the type of MW power applicator used, plasmas of a wide variety of geometries can be generated:

(a) Cylindrical MW plasmas of relatively small diameter can be created using rectangular or cylindrical resonant cavities (27), while long plasma columns of larger diameter can be generated with a variety of surface wave launchers (28,29),

- the surfatron,
- the Ro-box,
- the waveguide-surfatron,
- the surfaguide.

Large-diameter, short cylinders of MW plasma can also be created using various ECR reactor designs (section 3.2).

(b) In many present and future applications, it is desirable to create a planar MW plasma zone, for example for processing of flat panels (displays, solar cells), or possibly of future 300 mm wafers. This can be accomplished with a variety of linear MW power applicators, for example periodic slow wave structures (30,31), slotted waveguides (32), etc. In these cases the plasma is long, relatively narrow, and of limited depth perpendicular to the applicator; if a large-area substrate is to be treated uniformly, this obviously requires some form of relative motion (linear, rotational, planetary, ...) between the substrate and the plasma source (33).

3.2. ECR Reactors

As discussed in section 2.3., the presence of a static magnetic field B_0 can permit plasma enhancement and operation at very low gas pressures ($\lesssim$ 10 mTorr). This, in turn, can lead to very dense plasmas ($n \sim 10^{12}$ cm^{-3}, compared with $n \sim 10^{10}$ at 100 mTorr), hence to high ion-to-neutral ratios, an advantage in fine-line patterning (see section 4.1.). The Japanese were the first to use experimental ECR reactors as a substitute for reactive ion etching (RIE) (34-36); more refined ECR machines are now being installed on IC production lines, mostly in Japan.

There exist three main approaches to ECR reactor design, briefly described below:

(i) The waveguide ECR source, mostly divergent field systems (37), is the most common design: MW power enters the cylindrical discharge chamber through a dielectric window, and a set of magnetic coils create the ECR condition a few cm below the window. The resulting plasma "streams" into the adjacent process chamber, where the wafer is located. Since the B_0 field lines diverge, ion trajectories tend not to

be perpendicular to the wafer surface; this shortcoming can, however, be corrected by an appropriate electromagnet (or a set of permanent magnets) around the process chamber.
(ii) The multipolar, or so-called distributed ECR (or DECR) (38,39) also uses a cylindrical plasma chamber, but here a plurality of ECR plasma zones are created by rows of permanent magnets arranged axially along the chamber wall, combined with a cluster of appropriately-spaced linear MW antennae inside the chamber. At low pressure, the large mean free path of the constituent particles assures a very uniform plasma in the central region, where the wafer is located. Controlled ion bombardment of the wafer surface is achieved by separate RF biasing, and the B_0 field is negligible in the wafer region.
(iii) The so-called plasma disk ECR source (40) consists of a resonant MW cavity enclosing a fused silica vessel, with a multicusp B_0 field provided by permanent magnets around its lower end. This simple design is more compact than the ones described above.
(iv) Two types of planar ECR concepts have also been reported (38,41), for large-area surface treatment, beside the cylindrical ECR reactor designs (i) to (iii) above. Both use planar permanent magnets of "racetrack" geometry, but in the "DECR" case (38) the MW power is applied from an array of parallel linear antennae, while in the "EMG" (elongated mirror geometry) case (41) a large horn antenna is used.

4. Processing of Electronic Materials

4.1. Dry Etching and Resist Stripping

From the beginnings of the IC industry, increasing structural complexity and decreasing feature size have posed constant challenges to manufacturability (1-3,22,23); dry etching performance has therefore tended to be the principal driver for new concepts in plasma reactor design. For example, the 256 Mb DRAM, scheduled for production in 1998, will require feature sizes well below 0.5 µm on silicon wafers measuring 200 or 300 mm in diameter. The parallel plate and "hexode" RF plasma reactors of the 1980s have so far proven quite satisfactory; however, considerations of uniformity, minimum feature size, and "radiation damage" effects have led to alternate design concepts based on single wafer processing in highly dense plasmas: In sub-0.5µm technologies (for example, the 256 Mb DRAM), it is imperative that dry etching be carried out with extremely tight control of the critical dimensions, and with near-vertical profiles (in other words, with near-perfect anisotropy) (23). This may be accomplished by maximizing the contribution of ion-regulated (anisotropic) etch reactions, while limiting the isotropic radical reactions. Clearly, the ratio of ions to reactive neutrals n_i/N in the plasma must then be as high as possible (~0.1, compared with $\sim 10^{-3}$ in an RIE plasma). In addition, the ion energies must be tightly distributed about a mean value, which must be controllable over a wide energy range, and the ion trajectories must be perpendicular to the wafer surface. This, in turn, calls for a decoupling of the active species generation in the gas phase (that is, in the plasma bulk), and of the wafer potential (which governs the ion-regulated reactions).

ECR plasmas, in principle, possess many of the characteristics described above, and this partly explains the dramatic increase in R and D in this field in recent years (see, for example, ref. 3 and several chapters in refs. 9 and 10): Low pressure and high plasma density (see section 2.3.) assure a high n_i/N value, while wafer bias with a separate RF power source allows one to control plasma/surface interaction through ion bombardment (42,43).

However, Heidenreich et al. (16,44) have shown that RF bias can also yield anisotropic etching using a non-magnetized MW plasma at higher pressure, what we refer to as dual-frequency MW/RF plasma (25,26). They also showed that the MW/RF combination gives rise to synergism in O_2 plasma etching of polyimide, in that the etch rate was found to be substantially higher than the sum of the RF and MW etch rates measured separately.

As mentioned above, a substantial body of literature now exists which demonstrates the impressive potential of ECR to perform anisotropic etching of a wide variety of materials. However, as pointed out by Flamm (22), it has yet to be clearly established whether ECR sources bring any unique benefits. On the contrary, Cook and Donohoe (23) argue that etching at very low pressure (1 mTorr) greatly increases the capital expense of the apparatus due to the required large pump capacity, large vessel and connecting plumbing, and the hardware required to create the B_0 field. Instead, impressive sub-µm etch performance has also been demonstrated at higher pressures using enhanced planar reactors employing magnetrons or triodes, and with relatively newer RF plasma sources such as helical resonators (45), helicon (46), and inductively coupled reactors (47), which have been demonstrated capable of yielding high plasma densities ($\gtrsim 10^{12}$ cm^3).

Finally, dry "stripping" or "ashing" of photoresist is an important area of plasma etching in which the dominant consideration is not the control of minimum feature size, but to minimize potential sources of damage to the ICs (48). A proven method to accomplish this is to place the wafer "downstream" from the plasma source; here, only long-lived active species from the O_2 plasma (thought to be primarily O^1P oxygen atoms) contribute to the etch reaction, but not ions or u.v. photons which are potentially harmful to the ICs. In order to maximize the wafer throughput, a number of operating parameters must be optimized, namely power, pressure, flow rate, wafer temperature, etc. In a recent paper, McOmber et al. (49) describe the results of a study in which they used a commercial downstream asher to compare the relative efficiency of RF and MW plasma, all other system parameters being kept constant. Not only was the optimized MW operation found to yield faster ashing rates than the RF counterpart, but damage was also found to be reduced in the MW case (50).

4.2. Deposition of Thin Films

Plasma-enhanced chemical vapour deposition (PECVD) of thin films is vitally important for passivation layers, mask materials, dielectrics, conductors, etc., in VLSI and ULSI microelectronics on Si and III-V compound semiconductors (e.g. GaAs, InP, ...) (1,2). Electronic materials in the present context, however, also involve macroelectronic applications, where PECVD is of equal importance (4). These applications include photovoltaic energy sources, and large-area electronic devices for information technology such as electrophotographic receptors, photodiode arrays, and flat panel displays based on thin-film transistors. A key PECVD material in macroelectronics is hydrogenated amorphous silicon, a-Si:H, a semiconductor. These topics are all addressed in the excellent monograph by Mort and Jansen (4), which reviews the very extensive PECVD literature up to the mid-1980s.

As implied by the term PECVD, elevated substrate temperature T_s is generally needed to obtain high-quality deposits, but typical T_s values ($\approx$300°C) are much below those of "conventional" CVD processes ($\geq$ 700°C). It is, nevertheless, desirable to reduce T_s to even lower values without sacrificing film quality (if possible, to near ambient temperature, $T_s \approx 25$°C), for example in III-V semiconductor processing. In recent years this has given much impetus to PECVD research using MW-plasma techniques, particularly ECR (16,17): It is claimed that this approach results in less device damage than conventional PECVD techniques, for example when depositing plasma silicon nitride (P-SiN) passivation layers on III-V HFET devices (51).

Most ECR PECVD investigations compensate low T_s with appropriate RF-induced bias, since the resulting controlled ion bombardment is known to improve the film quality. A wide range of materials have been deposited this way, for example epitaxial silicon (52), silicon dioxide (P-SiO_2) (53), P-SiN (51,54), even metals such as copper (55), and several other types of films, too numerous to recite here (16). A possible advantage of ECR over higher pressure PECVD techniques may be a lesser tendency for gas-phase nucleation and growth of solid particles (56), on account of the large mean free paths at low pressure. We are currently unaware of any systematic study regarding this subject; however, as pointed out in section 4.1., the requirements of low pressure and magnetic field raise the cost of ECR equipment very substantially.

PECVD using non-magnetized MW plasmas at higher pressure (~100 mTorr) and elevated T_s can yield films of excellent quality, for example a-Si:H (57), P-SiN (58), P-SiO_2 and oxynitrides (P-SiON) (59). Comparable quality films of these same materials can, however, also be obtained at $T_s \approx 25$°C using the dual-frequency MW/RF approach (25,60,61), which avoids the inconveniences of ECR.

Finally, an important advantage of MW PECVD over its RF counterpart is higher film growth rate (12-14). Crystalline diamond, an electronic material of increasing importance, is deposited commercially almost exclusively by MW PECVD (62).

5. Conclusion

Processing of electronic materials with MW plasmas is a relatively new field, one which will undoubtedly witness important breakthroughs in coming years. The development of ECR techniques has created much justified enthusiasm, but the need for very low pressure and for magnetic fields significantly add to the process costs. Results of comparable quality, both in fine-line etching and in thin film deposition, have recently been demonstrated using new RF and MW (and dual-frequency MW-RF) higher pressure plasma techniques.

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References

1. T. Sugano, Ed., "Applications of Plasma Processes to VLSI Technology", Wiley-Interscience, New York, N.Y., (1989).
2. N.G. Einspruch and D.M. Brown, Eds., "Plasma Processing for VLSI", Vol. 8 in "VLSI Electronics Microstructure Science", Academic Press, Boston, MA (1984).
3. D.M. Manos and D.L. Flamm, Eds., "Plasma Etching — An Introduction", Academic Press, Boston, MA (1989).
4. J. Mort and F. Jansen, Eds., "Plasma Deposited Thin Films", CRC Press, Boca Raton, FL (1986).
5. F.K. McTaggart, "Plasma Chemistry in Electrical Discharges", Elsevier, Amsterdam, NL (1967).
6. J.P. Wightman, Proc. IEEE 62, 4 (1974).
7. Yu.A. Lebedev and L.S. Polak, High Energy Chem. 13, 331 (1979).
8. J. Musil, Vacuum 36, 161 (1986).
9. M. Moisan and J. Pelletier, Eds., "Microwave Excited Plasmas", Elsevier, Amsterdam, NL (1992).
10. C.M. Ferreira and M. Moisan, Eds., "Microwave Discharges — Fundamentals and Applications", NATO ASI Series, Series B: Physics Vol. 302, Plenum, New York, N.Y., (1993).
11. D.L. Flamm, J. Vac. Sci. Technol. A4, 729 (1986).
12. M.R. Wertheimer and M. Moisan, J. Vac. Sci. Technol. A3, 2643 (1985).
13. M. Moisan, C. Barbeau, R. Claude, C.M. Ferreira, J. Margot, J. Paraszczak, A.B. Sá, G. Sauvé, and M.R. Wertheimer, J. Vac Sci. Technol. B9, 8 (1991).
14. M. Moisan and M.R. Wertheimer, Surface and Coatings Technol. (in press).
15. E.M. Liston, L. Martinu and M.R. Wertheimer, J. Adhesion Sci. Technol. (in press).
16. J. Paraszczak and J. Heidenreich, Chapt. 15, p. 435, in ref. 9.
17. J. Paraszczak and J. Heidenreich, p. 445 in ref. 10.
18. C.M. Ferreira and M. Moisan, Physica Scripta 38, 382 (1988).
19. C.M. Ferreira, M. Moisan, and Z. Zakrzewski, Chapt. 2, p. 25, in ref. 9.
20. C.M. Ferreira and J. Loureiro, J. Phys. D.: Appl. Phys. 22, 76 (1989).
21. C.M. Ferreira, L.L. Alves, M. Pinheiro, and A.B. Sá, IEEE Trans. Plasma Sci. 19, 229 (1991).
22. D.L. Flamm, Solid State Technol. Mar. 1991, p. 47.
23. J.M. Cook and K.G. Donohoe, Solid State Technol. Apr. 1991, p. 119.
24. B. Chapman, "Glow Discharge Processes", Wiley-Interscience, New York, N.Y. (1980).
25. M.R.Wertheimer and L. Martinu, p. 465 in ref. 10.
26. O.M. Küttel, J.E. Klemberg-Sapieha, L. Martinu, and M.R. Wertheimer, Thin Solid Films. 193/194, 155 (1990).
27. F.C. Fehsenfeld, K.M. Evenson, and H.P. Broida, Rev. Sci. Instrum. 36, 294 (1965).
28. M. Moisan and Z Zakrzewski, Chapt. 5, p. 123, in ref. 9.
29. M. Moisan and Z Zakrzewski, J. Phys. D: Appl. Phys. 24, 1025 (1991).
30. R.G. Bosisio, C.F. Weissfloch, and M.R. Wertheimer, J. Microwave Power 7, 325 (1972).
31. R.G. Bosisio, M.R. Wertheimer, and C.F. Wessfloch, J. Phy. E: Sci. Instrum. 6, 628 (1973).
32. G. Sauvé, M. Moisan, and Z. Zakrzewski, J. Microwave Power, submitted (1993).
33. B. Lamontagne, A.M. Wróbel, G. Jalbert, and M.R. Wertheimer, J. Phys. D: Appl. Phys. 20, 844 (1987).
34. Y. Okamoto and H. Tamagawa, Rev. Sci. Instrum. 43, 1193 (1972).
35. K. Suzuki, S. Okudaira, N. Sakudo, and I. Kanomota, Jap. J. Appl. Phys. 16, 1979 (1977).
36. K. Suzuki, S. Okudaira, and I. Kanomota, J. Electrochem. Soc. 126, 1924 (1979).
37. J.M. Cook, D.E. Ibbotson, P.D. Foo, and D.L. Flamm, J. Vac. Sci. Technol. A8, 1820 (1990).
38. M. Pichot and J. Pelletier, Chapt. 14, p. 419, in ref. 9.
39. M. Pichot, A. Durandet, J. Pelletier, Y. Arnal, and L. Vallier, Rev. Sci. Instrum. 59, 1072 (1988).
40. L. Mahoney, M. Dahimene, and J. Asmussen, Rev. Sci. Instrum. 59, 448 (1988).

41. M. Geisler, J. Kieser, E. Räuchle, and R. Wilhelm, J. Vac. Sci. Technol. A8, 908 (1990).
42. J. Pelletier and M.J. Cooke, J. Appl. Phys. 65 464 (1989).
43. O. Joubert, J. Pelletier, and Y. Arnal, J. Appl. Phys. 65, 5096 (1989).
44. J. Heidenreich, J. Paraszczak, M. Moisan, and G. Sauvé, Microelec. Eng. 5, 363 (1986).
45. J.M. Cook, D.E. Ibbotson, and D.L. Flamm, J. Vac. Sci. Technol. B8, 1 (1990).
46. R.W. Boswell and D. Henry, Appl. Phys. Lett. 47, 1095 (1985); A.J. Perry and R.W. Boswell, Appl. Phys. Lett. 55, 148 (1989).
47. J.A. O'Neill, M.S. Barnes, and J.H. Keller, J. Appl. Phys. 73, 1621 (1993).
48. D.L. Flamm, Solid State Technol., Sept. 1992, p. 43.
49. J.I. McOmber, J.T. Davies, J.C. Howden, M. Wright, and K.D. Saul, Proc. 9th Int. Plasma Processing Symp., The Electrochem. Soc., PV92-18, p. 480 (1993).
50. S.A. Bell and D.W. Hess, J. Electrochem. Soc. 139, 2904 (1992).
51. D.J. Newson, A.J. Murrell, R.C. Grimwood, and I.D. Henning, Electronics Lett. 29, 472 (1993).
52. R. Burke, J. Pelletier, C. Pomot, and L. Vallier, J. Vac. Sci. Technol. A8, 2931 (1990).
53. O. Joubert, R. Burke, L. Vallier, and C. Martinet, Appl. Phys. Lett. 62, 228 (1993).
54. K.A. Buckle, J. Rodgers, K. Pastor, C. Constantine, and D. Johnson, Appl. Phys. Lett. 60, 2601 (1992).
55. J. Pelletier, R. Pantel, J.C. Oberlin, Y. Pauleau, and P. Gouy-Pailler, J. Appl. Phys. 70, 3862 (1991).
56. K.G. Spears, T.J. Robinson, and R.M. Roth, IEEE Trans. Plasma. Sci. PS-14, 179 (1986).
57. L. Paquin, D. Masson, M.R. Wertheimer, and M. Moisan, Can. J. Phys. 63, 831 (1985).
58. Y. Tessier, J.E. Klemberg-Sapieha, S. Poulin-Dandurand, M.R. Wertheimer, and S.C. Gujrathi, Can. J. Phys. 65, 859 (1987).
59. S. Blain, J.E. Klemberg-Sapieha, M.R. Wertheimer, and S.C. Gujrathi, Can. J. Phys. 67, 190 (1989).
60. L. Martinu, J.E. Klemberg-Sapieha, and M.R. Wertheimer, Appl. Phys. Lett. 54, 2645 (1989).
61. J.E. Klemberg-Sapieha, O.M. Küttel, L. Martinu, and M.R. Wertheimer, Thin Solid Films 193/194, 965 (1990).
62. R.E. Clausing, L.L. Horton, J.C. Angus, and P. Koidl, Eds., "Diamond and Diamond-Like Films and Coatings", NATO ASI Series, Series B: Physics Vol. 266, Plenum, New York, N.Y. (1991).