AXIC APPLICATION REPORT

PLASMA ENHANCED CVD

14

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THERE ARE SEVERAL PLASMA INVOLVED TECHNIQUES FOR THIN FILM DEPOSITION. Their mechanism may occur in different ways with dependence on the technique, gas and process condition:

1. ***Transport of target material to substrate*** is provided by interaction of plasma (almost ions) with target (e.g. reactive ion sputtering), sputtered atoms may undergo chemical reactions on the target or occurs in the plasma volume, and subsequent transport of product material to the substrate makes material to be deposited into a thin film (Fig. 1-a).

2. ***Modification of substrate material in a plasma***, e.g. processes as plasma oxidation, nitridation or carbidization of the substrate (it depends on the operating gas: O_2, N_2 and gases with a content of C) due to the penetration of atoms into a subsurface region may provide production of very thin layers 5 - 25 Å (see Fig. 1-b).

3. ***Production of polymer films*** during plasma polymerization from hydrocarbons (Fig. 1-c) due to high density of unsaturated radicals in the plasma, difussion of the radicals to surface, followed by adsorption and migration onto the surface and bonding into thin polymer films produces many very desirable physical properties.

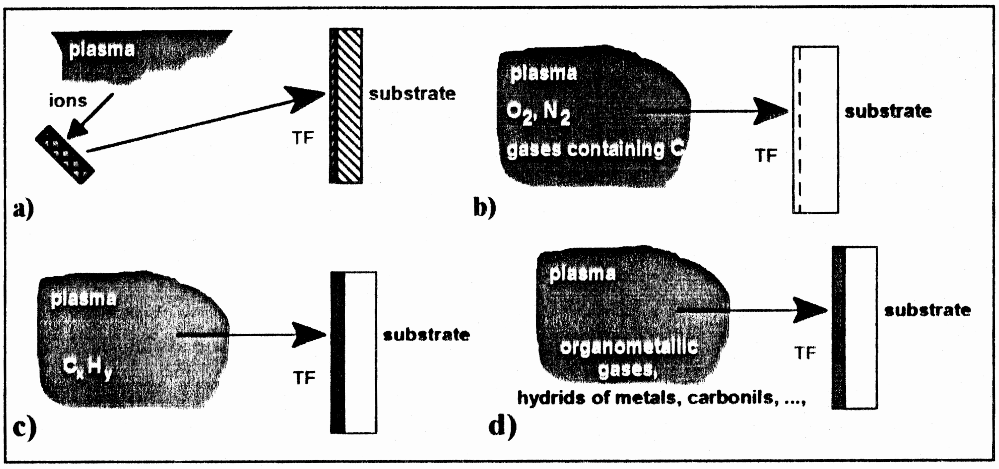

FIG. 1

Schematics of deposition mechanism: (a) sputter deposition from target, (b) plasma oxidation, nitridation or carbidization, (c) plasma polymerization and (d) plasma enhanced CVD.

4. ***Production of thin films by Plasma Enhanced CVD*** (Fig. 1-d) is important low temperature deposition process in microelectronics, optoelectronics, micro-mechanics and sensorics. This process produces high deposition rates, good adhesion, low deffect density, good covering and planarization behaviour, good electrical properties of oxides and nitrides, useful for passivation of Al-metallization structures, etc. Scheme of PECVD reactor is shown in Fig. 2.

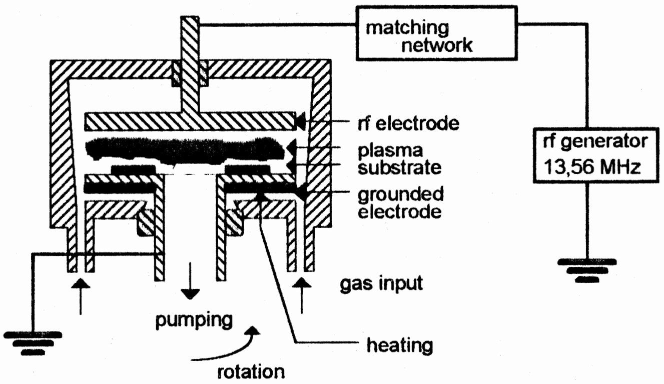

FIG. 2
Principal scheme of PE CVD reactor.

PHYSICS AND CHEMISTRY IN PECVD

What is the plasma enhanced CVD method? ***Chemical vapor deposition (CVD)*** consists of a reaction in which two reagents in gas phase C(g) and D(g) undergo the reaction at the atmospheric or reduced pressure and high temperature (up to 1200 °C), as result the solid A(s) and gas volatile B(g) products are produced:

$$C(g)+D(g)\ \underset{\substack{high\\ temperature\\ \geq 800°C}}{\longrightarrow}\ A(s)+B(g)$$

Plasma enhanced CVD is a reaction of two reagents in gas phase at low temperature plasma environment:

$$C(g)+D(g)\ \underset{\substack{low-temperature\\ plasma}}{\longrightarrow}\ A(s)+B(g)$$

Lower process temperature allows reduction of the substrate degradation. Precipitation temperature is different for these processes (Table 2).

Table 1
Deposition of silicon nitride can be produced by reactions:

CVD	$3SiH_4(g)+4NH_3(g)\ \xrightarrow[700-800°C]{\substack{atmospheric\\ pressure}}$ $\rightarrow Si_3N_4(s)+12H_2(g)$
PE CVD	$3SiH_4(g)+4NH_3(g)\ \xrightarrow[300-500°C]{\substack{lowtemperature\\ plasma}}$ $\rightarrow Si_3N_4(s)+12H_2(g)$

Tab. 2
Precipitation temperature for several materials.

Mate-rial	Reaction componets	Temperature of precipitation (°C)	
		atmospheric CVD	*plasma enhanced CVD*
Si_3N_4	SiH_4,NH_3(N_2)	700-900	300-500
SiO_2	SiH_4,N_2O	900-1200	200-300
Al_2O_3	$AlCl_3$,O_2	700-1000	100-500
TiN	$TiCl_4$($TiCl_4$)-N_2(N_2+H_2)	1300	300

The reduction of process temperature can be explained by follows: In a low temperature plasma an energy of electrons is much higher than temperature of the ions and neutrals, that means the chemical reaction can flow at lower gas temperature with the same rate constant (Fig. 3).

Characteristics of PECVD systems:

- usually systems with internal electrodes,
- parallel electrodes, rotative motion,
- heating of electrodes,
- diameter of electrodes is 3-60 cm, distance ≈ 5-10 cm,
- radial gas flow,
- tunning network: connected through coil - no self bias potential.

Voltage: AC signal in range from 40 kHz to 2.45 MHz with amplitude of several hundred volts, typical electron density in plasma is $n_e \approx 10^9$-10^{12} cm^{-3}.

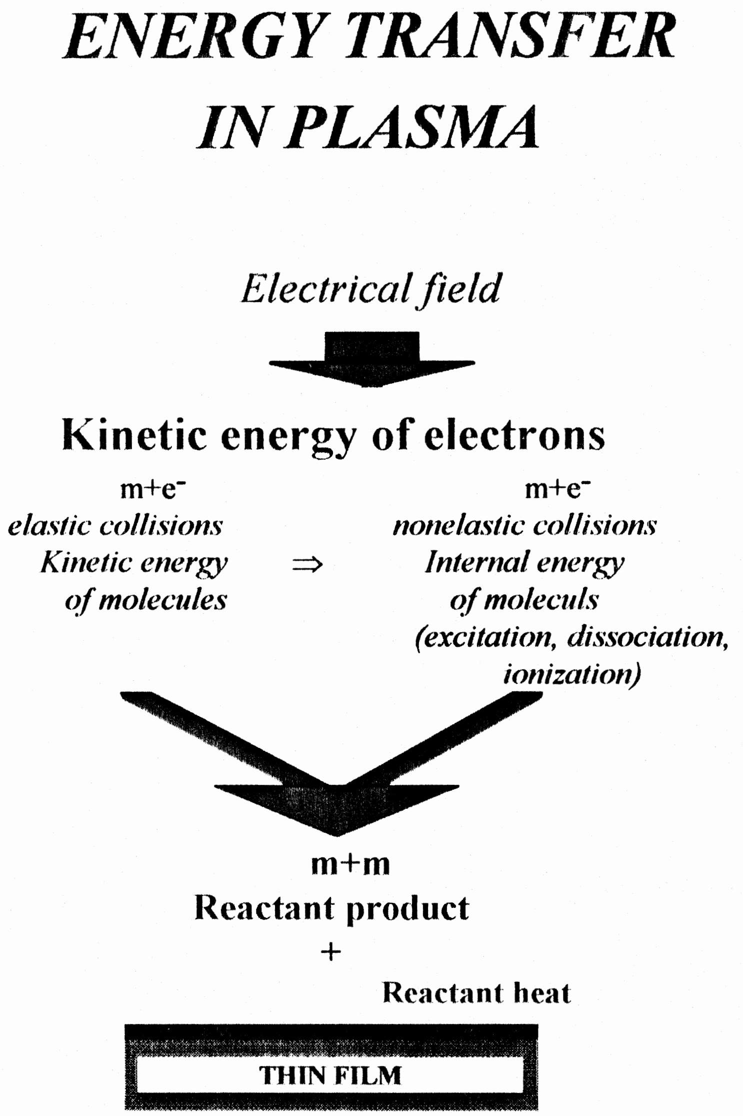

FIG. 3
Diagram of energy flow in plasma.

Tab. 3
Elemental processes in plasma during deposition.

Ionization	$A_2 + e \rightarrow A_2^+ + 2e$
Dissociative ionization	$A_2 + e \rightarrow A^+ + A + 2e$
Dissociation of molecules	$A_2 + e \rightarrow 2A + e$
Excitation of energy levels	$A_2 + e \rightarrow A_2^* + e$
Dissociative attachment of electrons	$A_2 + e \rightarrow A^- + A$

Note: A_2 *- molecule,* A *- atom,* A^+ *- atomic ion,* A_2^+ *- molecular ion,* A^* (A_2^*) *- excited atom (molecule).*

Deposition process has several steps:

1) ***generation of radicals and ions in discharge***
2) ***adsorbtion of radicals and ions on surface***
3) ***redistribution on surface***

PLASMA DEPOSITION (PE CVD) OF DIELECTRIC THIN FILMS

Properties of PECVD silicon nitride:

Typical reaction is:

$$SiH_4 + NH_3(or \bullet N_2) \xrightarrow[rf\ plasma]{200-400^\circ C} Si_xN_yH_z + H_2$$

which is occuring in several steps:

$$SiH_4 \xrightarrow{4{,}07 eV} SiH_3 + H$$

$$SiH \xrightarrow{3{,}09 eV} Si + H$$

$$NH_3 \xrightarrow{4{,}76 eV} NH_2 + H$$

$$NH_2 \xrightarrow{3{,}9 eV} NH + H$$

$$NH \xrightarrow{3{,}42 eV} N + H$$

$$N_2 \xrightarrow{9{,}83 eV} 2N$$

Composition, deposition rate and other properties depends on pressure, power, gas mixture and reactor configuration. Typical stoichiometry is 18-22 at. % of hydrogen, 2-13 at. % of oxygen, refraction index $\approx 2.00 \pm 0{,}05$, ratio Si:N = 0.73-1.20.

Properties of PECVD silicon oxide:

The film is usually prepared by reaction:

$$SiH_4 + 2NO_2 \xrightarrow[rf \bullet plasma]{200-400^\circ C} SiO_2 + 2N_2 + 2H_2$$

or

$$SiH_4 + O_2 \xrightarrow[rf \bullet plasma]{200-400^\circ C} SiO_2 + 2H_2$$

Plasma oxide has refraction index n=1.46-1,52, contains about 5 - 10 at. % of hydrogen and 2 at. % of nitrogen in a form of compounds like SiH, SiOH or H_2O. Plasma silicon oxynitride - $SiO_xN_y(H_z)$ can be prepared by the similar process.

REFERENCES

[1] Grill, A., *Cold Plasma in Materials Fabrication*, IEEE, New York (1994) 153-166

[2] Rossnagel, S.M., Cuomo, J.J. and Westwood, W.D.: Handbook of Plasma Processing Technology. Noyes Publications, Park Ridge, NJ (1990).

[3] Brcka, J., PECVD Applications, in: Plasma Application Report, AXIC, Santa Clara, CA (1996).

SILICON NITRIDE - Si_3N_4

Refractive index = 2.00

D (Ang.)	COLOR		D (Ang.)	COLOR		D (Ang.)	COLOR	
200 - 400	░	"silicon-like" color	1000 - 1100	■	very bright blue	1900 - 2100	■	dark red
400 - 530	░	gold-to-brown	1100 - 1200	░	"silicon-like" color	2100 - 2300	■	blue
530 - 730	■	red	1200 - 1300		bright yellow	2300 - 2500	■	blue-to-green
730 - 770	■	darkbrown	1300 - 1500		dark yellow	2500 - 2800	░	light green
770 - 930	■	blue	1500 - 1800	▓	orange-to-red	2800 - 3000	▓	orange-to-yellow
930 - 1000	▓	bright-blue	1800 - 1900	■	red	3000 - 3300	■	red

SILICON DIOXIDE - SiO_2

Refractive index = 1.45

D (Ang.)	COLOR		D (Ang.)	COLOR		D (Ang.)	COLOR	
200	░ [1]	darker silicon	2800	■	violet	5400	■	dark green
400	░	yellow-to-brown	3000	■	violet-to-blue	5600	■	bright green
600	▨	brown-to-goldbrown	3200	■	blue-to-violet	5800	▨	light green
800	■	darkbrown	3400	■	bright blue	6000	░	very light green
1000	■	blue	3600	■	green	6200	▨	slightly getting red
1200	■	bright-blue	3800	▨	yellow-to-green	6400	■	bright red
1400	▨	very bright blue	4000	░	lemon green	6600	■	red
1600	░	"silicon-like" color	4200	▨	yellow-to-violet	7000	■	violet-to-red
1800		yellow	4400	▨	bright violet	7200	▨	violet-to-green
2000		bright-yellow	4600	▨	violet	7400	▨	green-to-violet
2200		dark yellow	4800	■	darker violet	7600	░	bright green
2400	▨	yellow-to-violet	5000	■	dark violet			
2600	▨	violet-to-yellow	5200	■	violet-to-green			

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[1] *The colors here are printed by color printer and may be different from real tone in dependence on light source.*