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PLASMA-DEPOSITED SILICON NITRIDE FILMS IN HMDS (HEXAMETHYLDISILAZANE) VAPOURS[1])

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Thin silicon nitride films are deposited in the rf discharge plasma of hexamethyldisilazane (HMDS) and nitrogen vapours. The resulting Si_xN_y films with a refractive index 1.6—2.1 are chemically very stable and suitable for some special techniques ("lift off"). The silicon nitride films composition and properties have been investigated in dependence on the deposition conditions.

О ПЛЕНКАХ НИТРИДА КРЕМНИЯ, НАПЫЛЯЕМЫХ ПЛАЗМЕННЫМ ПУТЕМ В ПАРАХ ГЕКСАМЕТИЛДИСИЛАЗАНА

Пленки нитрида кремния напылялись в высокочастотной газорязрядной плазме, состоящей из паров гексаметилдисилазана и азота. Полученные пленки Si_xN_y с показателем преломления 1,6—2,1 оказались химически очень устойчивыми и подходящими для некоторых специальных технологий. Исследовались также состав и свойства пленок нитрида кремния в зависимости от условий напыления.

I. INTRODUCTION

Silicon nitride (Si_3N_4) has become well known as an insulating and passivating layer for semiconductor devices. The plasma enhanced deposition technology (PE CVD) of Si_xN_y films at low temperature to avoid damaging devices has become of increased interest. The plasmochemically produced silicon nitride films are deposited on silicon wafers in rf plasma capacitively generated at a temperature 100—400 °C and a pressure 20—200 Pa. These earlier methods of depositing the silicon nitride have used the silane (SiH_4) vapour mixed with nitrogen or a gaseous nitrogen compound such as ammonia [1, 2]. However, SiH_4 is an extremly reactive, dangerous compound. It reacts violently with air, water, etc. to produce silicon oxides which degrade the nitride layer.

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Vaporizable silicon-nitrogen compounds as HMDS: $[(CH_3)Si]_2NH$, AZS: $(CH_3)_3SiN_3$ (azidotrimethylsilane) may, however, be used and decomposed in the plasma discharge, depositing a film of silicon nitride on the exposed surface [3—6].

II. EXPERIMENTAL

A schematic drawing of the experimental setup is presented in Fig. 1. The discharge tube of simax glass (internal diameter 8 cm, tube length 40 cm) was externally heated by the resistance wire. Both ends of the discharge tube had been provided by flanges with rubber sealing. One flange (the exit flange) was connected through the cold trap with the standard oil pump (20 m^3 per hour). The second (inlet) flange was provided by a removable cover with the sight-quartz window and connectors of the generator.

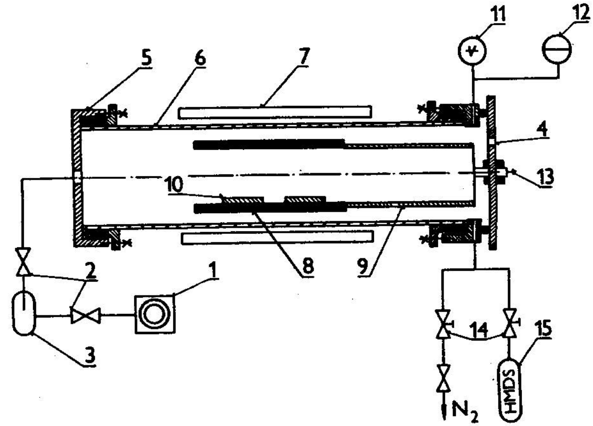

Fig. 1. A schematic drawing of the experimental equipment: 1 — the oil pump, 2 — valves, 3 — cold trap, 4 — quartz window for spectroscopical observation, 5 — exit flange, 6 — discharge tube, 7 — external heating, 8 — graphite slab, 9 — ceramic holder, 10 — substrate, 11 — Pirani vacuum gauge, 12 — Baratron vacuum gauge, 13 — the connector to the rf power input, 14 — needle valves, 15 — vessel with monomer.

The reactant gases were introduced at a fixed flow rate through the inlet flange. The pressure was continuously measured by a Pirani vacuum gauge on the inlet flange. The reactor internal configuration consists of two graphite slabs electrically insulated from one another by teflon spacers. Silicon wafers are placed in pockets on the internal sides of graphite slabs.

The 1.5 MHz rf power input (70 W max.) was fed to the graphite slabs so that the uniform plasma field could be set up in each space between the slabs. A fixed

flow of reactant gases, HMDS vapour and nitrogen was established using the system of regulating needle valves. Before each run the discharge tube was exhausted to the pressure of 1 Pa. The light emitted from the capacitively coupled system was detected by the monochromator with a EMI-6255 B photomultiplier. The light signals detected by the photomultiplier were recorded by the chart recorder. The index of refraction and the silicon nitride film thicknesses were measured by the ellipsimetric method. The absorption and reflection IR spectra and the Raman spectra of deposited layers were measured using the Perkin-Elmer spectrophotometer and the Spex Ramalog 3.

III. RESULTS

In the experimental work the main attention was paid to the preparation of thin films having a composition and properties similar to those of Si_3N_4, of which the

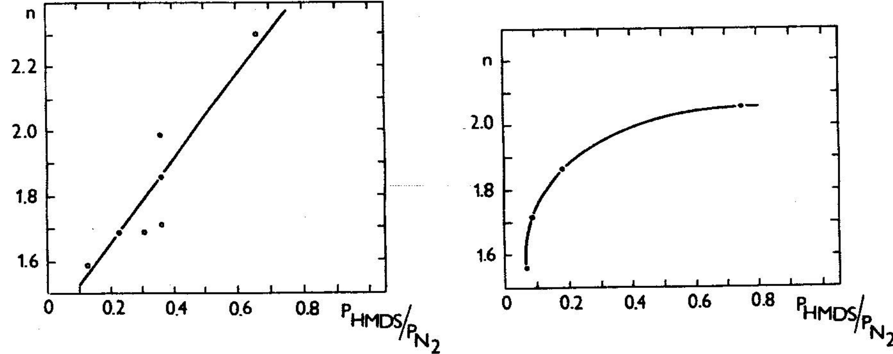

Fig. 2. The index of refraction of silicon nitride films vs. the pressure ratio p_{HMDS}/p_{N_2} (2a — substrate temperature 120 °C, 2b — substrate temperature 90 °C).

refractive index 2.0—2.1 is characteristic. The next no less important requirement consists in obtaining an adequate homogeneity in both the thickness and the refractive index of one deposition run.

As expected, the kinetics of growth and the properties of silicon nitride films proved to be strongly dependent on deposition parameters. It was found that the refractive index was increasing with the raising of the partial pressure and the flow of the HMDS. The best results were obtained at the partial pressure ratio of HMDS and N_2: $p_{HMDS}/p_{N_2} = 0.35 - 0.40$ (Fig. 2). The optimum total pressure was found to be in the interval from 5—25 Pa. The range of substrate temperatures studied in our investigation with HMDS was 25—150 °C. The refractive index values

measured in samples of substrate temperature exceeding 90 °C are generally higher than those samples of lower substrate temperature. The silicon nitride films deposited at lower temperatures (25—80 °C) are soft and similar to the films prepared by the plasma polymerization method. With the increase in the substrate temperature the hardness of Si_3N_4 films is substantially higher and the silicon nitride becomes more stoichiometric.

The growth rate of silicon nitride films is dependent on the specific power input [W/cm^3], the flow rate of HMDS and N_2, the homogeneity of the rf discharge and the so-called "residence time" of the reactant in the discharge region. The growth rates measured during our investigation of Si_xN_y films from HMDS were 10—50 nm/min. The sufficient rf power input per volume unit of the discharge reaches 0.15—0.25 W/cm^3 only.

IV. CHEMICAL PROPERTIES

The etch rate of silicon nitride films prepared from HMDS were determined for a 3 : 4 : 12 $NH_4HF_2/NH_4F/H_2O$ solution and H_3PO_4. The silicon nitride from HMDS in these solutions is practically insoluble. The etch rate was also evaluated in the rf plasma system at the pressure of 260 Pa (150 W) with the etch gas mixture created by $CF_4 + O_2$ (15 %). The etch rates in the rf plasma are generally higher (10—20 nm/min), since the composition of silicon nitride films prepared in rf plasma from HMDS may be represented by $Si_xN_yH_zC_w$. It is possible that the unexpected chemical inertness of the silicon nitride films is due to the incorporation of CH_3, CH groups. Some evidence of the presence of a CH group was found by the IR spectrometry.

V. OPTICAL EMISSION FROM THE RF PLASMA DURING THE DEPOSITION OF SILICON NITRIDE FILMS

The spectroscopic analysis of the optical emission during the deposition of silicon nitride films was used to obtain a better understanding of the plasma chemistry involved in this system. The optical emission was studied in an $HMDS + N_2$ gas mixture. The analysis was carried out between 200 and 650 nm. In the spectra the following atomic and molecular spectra were identified [7, 8]:

1) H_β – 486.1 nm, H_γ – 434.0 nm, SiI – 288.1 nm

2) N_2 second positive system ($C^3\Pi \rightarrow B^3\Pi$), N_2^+ main system ($^2\Sigma \rightarrow {}^2\Sigma$ ground state), CH – Q head of a (0.0) band — 431.2 nm (4300 A. System), CN — violet system ($^2\Sigma \rightarrow {}^2\Sigma$ ground state) — 388.3 nm; 387.1 nm; 386.1 nm.

By increasing the partial pressure ratio of HMDS and N_2 (p_{HMDS}/p_{N_2}) it is possible to notice the relative intensity decrease of maxima in accord with a molecular nitrogen spectrum (systems N_2, N_2^+) and the relative intensity growth of

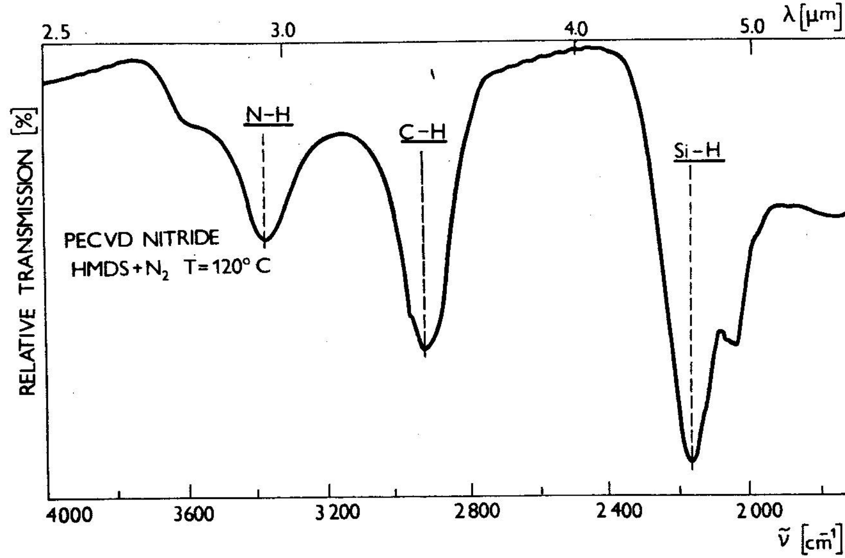

Fig. 3. MIR spectra of PE CVD nitride thin films prepared from $HMDS + N_2$.

both the H_β, H_γ and SiI atomic lines and the CH, CN systems maxima. On the face of it the dissociation of CH_3 groups and N–H bond decay accompanied by a greater H concentration and Si–C, Si–NH–Si bonds rupture which give rise to SiI pass after the introduction of HMDS into the discharge. Simultaneously, the originating fragments are combined by the releasing bonds (CN system). However, no structure of the SiN system has been identified in the emission spectra. Thus, it can be concluded that the Si–N bonds, whose existence was proved by the IR spectra, may be created on the activated substrate surface. Hence, the heterogeneous processes dominate during deposition in this case.

VI. INFRARED SPECTRA OF SILICON NITRIDE FILMS

The nitride films were deposited on two-sided optically polished silicon wafers, the reference sample being represented by the same clean silicon wafer without a deposited layer. The reflection (MIR) spectra are given in Fig. 3. The silicon nitride films were also deposited on a single crystal silicon plate of trapezoidal section. The number of reflections produced in the silicon nitride layer amounts to 50. A shift in the maximum absorption peak to the shorter wavelengths is generally observed with increasing substrate temperature. All samples of the liquid HMDS were also analysed using the methods of absorption IR spectroscopy.

The IR spectrum exhibits the absorption bands 765, 1190, 3375 cm^{-1} for the HN bond in the Si–HN–Si system, then 565, 940 cm^{-1} for SiN bond in the Si–N–Si system and a series of SiC, $SiCH_3$ respectively, from which the strongest one lies with 840, 1260 cm^{-1}. The IR spectra of monomers (HMDS) are qualitatively the same. However, they differ in the absorption intensity at 1065 cm^{-1}, which is associated with the Si–O bond occurring due to the hydrolytical contamination by air humidity. The partially hydrolyzed monomer thus introduces the Si–O bond into the silicon nitride. The IR absorption spectrum of the deposited silicon nitride differs substantially from that of the monomer (HMDS). The fundamental changes in the IR spectra may be characterized as following:

1) The absorption bands are broadened, which proves the presence of "inorganic bonds" of Si–O, Si–N, Si–C [9].

2) The intensity of methylsilyl bands (1260 cm^{-1}) decreases and the absorption shifts to 840—810 cm^{-1}, showing the reduced number of CH_3 substituents and an increased Si–Si bonds concentration.

3) The bands for the NH bonds are lessened substantially.

4) The wide absorption for 1050 cm^{-1} corresponding evidently to Si–O structures appears dominant. Oxygen originates not only from the partially hydrolyzed monomer, but also from the impure gaseous inert (N_2) [10].

5) The MIR spectra, however, show the silicon nitride prepared from the HMDS + N_2 in the rf plasma to involve the NH, CH and SiH groups.

The silicon nitride films for the Raman spectroscopy were deposited on nickel plates. The incident Ar laser light beam makes the angle of 45° with the sample surface. The observed Raman spectra are complicated and besides the characteristic groups and bonds determined by the IR spectroscopy also show the presence of multiple NH and CN bonds.

VII. CONCLUSION

Thin silicon nitride films were prepared in the capacitively coupled rf discharge plasma of hexamethyldisilazane and nitrogen vapours. The mechanically hardest and chemically most resistant films with a refractive index 1.6—2.1 were obtained for the pressure ratio $p_{HMDS}/p_{N_2} = 0.35$—0.40. The growth rates of silicon nitride layers have varied from 10—50 nm/min dependent upon the experimental conditions. The nitride films of desirable properties were prepared from the gas mixture HMDS + N_2 at relatively low temperatures (90—130 °C) in comparison with the currently used mixture $SiH_4 + N_2$. This advantage can favourably be employed in the "lift off" technique of preparing the integrated circuits. Moreover, HMDS is a much less reactive compound if compared to silane SiH_4 and the operation with it is more safe. However, the hydrolytical contamination of HMDS may quickly occur by air humidity if exposed to the air. The chemically bonded

oxygen is then incorporated into the nitride layer which is shown by IR spectra. The analysis of the optical spectra of plasma leads to the conclusion that heterogeneous processes dominate during the deposition.

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