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(19) THE PATENT OFFICE LONDON

(54) PHOSPHORUS-NITROGEN-OXYGEN FILM AND METHOD FOR MAKING SUCH FILM

(71) We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York in the United States of America, of Armonk, New York 10504, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to phosphorus-nitrogen-oxygen film and a method of making such film.

Phosphorus and nitrogen compositions have been known and are described, for example, in U.S. Patents 1,634,795, 2,884,318, 3,859,418 and 3,931,039. The principal use of these nitride materials have been in fertilizers or plant foods. Another proposed use was as a diffusing source for phosphorus into silicon wafers to produce N-type regions in the production of semiconductor devices such as transistors and integrated circuits. It has been in this context that U.S. Patent 3,931,039 describes in its prior art a method for forming a phosphorus nitride coating. It is pointed out in this patent that the phosphorus nitride coating is thermally unstable and readily decomposes. The patent goes on to described a method for forming a thermally stable phosphorus nitride-silicon dioxide composition which is usable as a diffusion source of N-type impurities for the formation of semiconductor devices.

According to the invention there is provided a method of forming an amorphous phosphorus-nitrogen-oxygen film comprising providing a reaction chamber with a substrate disposed therein, said chamber having a substrate temperature from 400° to 900°C, passing reaction gases PH_3, NH_3 and a gas which is a source of oxygen through the chamber to deposit onto said substrate a film of phosphorus-nitrogen-oxygen material having a formula $(P_x N_y O_z)$ wherein x is from 30 to 32 atomic percent, y is from 36 to 48 atomic percent and z is from 21 to 33 atomic percent.

Further according to the invention there is provided a substrate having a coating of amorphous phosphorus-nitrogen-oxygen material having a formula $(P_x N_y O_z)_n$, wherein x is from 30 to 32 atomic percent, y is from 36 to 48 atomic percent and z is from 21 to 33 atomic percent.

According to the invention further there is provided a semiconductor electronic structure comprising a silicon body having semiconductor devices therein and a coating of amorphous phosphorus-nitrogen-oxygen material over at least a portion of one surface thereof, said material having a formula $(P_x N_y O_z)_n$, wherein x is from 30 to 32 atomic percent, y is from 36 to 48 atomic percent and z is from 21 to 33 atomic percent.

The invention will now be described by way of example with reference to the accompanying drawings in which:-

Figure 1 illustrates one form of reaction chamber for manufacturing the composition of the present invention:

Figures 2 and *3* illustrate structures in using the composition of the present invention in electronic semiconductor structures;

Figure 4 is a graphical representation of the formation region of the composition as it is dependent upon the oxygen source concentration in the feed gaseous mixture versus the deposition temperature;

Figure 5 illustrates the effect of deposition temperature upon deposition rate;

Figure 6 shows compositions of P-N-O and boron doped P-N-O coatings fabricated at

650°C.;

Figure 7 compares the dielectric constant versus deposition temperature of the composition of the present invention with that of silicon nitride;

Figure 8 shows the relationship between the deposition temperature of the material of the present invention versus the refractive index of the resulting coating; and

Figure 9 illustrates the etch rate of coatings with H_2SO_4 at temperatures from 100°C to 230°C.

Figure 1 illustrates the apparatus for forming the amorphous phosphorus-nitrogen-oxygen material of the present invention. The apparatus includes a fused quartz (silicon dioxide) reactor tube 10. Surrounding the reactor wall is an induction heating coil 12 for heating the reactor and anything therein. Within the reactor is a graphite susceptor 14 which is enclosed in a fused quartz (silicon dioxide) envelope 16. Substrates 18 such as silicon semiconductor wafers are positioned over the graphite susceptor. The temperature of the substrates 18 are raised by RF induction heating process until the substrate temperature is between about 400-900°C. The reaction gases containing phosphorus, nitrogen and oxygen source are then passed through the chamber where the deposition of the amorphous phosphorus-nitrogen-oxygen material occurs onto the substrates 18. The preferred gases are phosphine (PH_3), ammonia (NH_3) and oxygen (O_2) with nitrogen carrier gas.

Examples of the resulting structures are shown in Figures 2 and 3. Figure 2 illustrates a silicon wafer 20 having a silicon dioxide coating 22 thereon and a phosphorus nitrogen oxygen coating of the present invention 24 over the silicon dioxide coating 22. Figure 3 illustrates a silicon substrate 20 having the phosphorus nitrogen oxygen coating 24 of the present invention directly on the silicon substrate. Semiconductor devices may be formed within the silicon substrate 20 and the coating 24 can act either as a passivating coating or a masking coating for diffusion or ion implantation steps.

The presence of oxygen in the resulting phosphorus nitrogen product is critical so that the coating will adhere properly to substrates and will be stable and not be decomposed as would oxygen free coatings of phosphorus nitride at ordinary temperatures. Oxygen is preferably brought into the compound by the addition of oxygen gas to the reaction gases. The addition of oxygen also rapidly promotes the deposition rate.

Figure 4 illustrates the formation region of the phosphorus nitrogen oxygen amorphous composition over the deposition temperature range of about 400-900°C. The oxygen concentration in the feed gaseous mixture is from 0.01 to about 98% excluding the ammonia and phosphine. The crosses indicate data points where good adhering and stable coatings were formed. The squares indicate points of no deposition of the material of the present invention. The gaseous materials for deposition of the coating of phosphorus-nitrogen-oxygen are ammonia, phosphine and oxygen. This is because such gases are available in high purity and in simple molecular form. Consequently, undesirable side reactions can be minimized. Furthermore, source materials in gaseous state provide the great easiness for CVD process control. Suitable carrier gases in addition to nitrogen are He, Ar, and other inert gases or mixtures thereof.

Referring to Figure 5, there is shown the deposition rate in Angstroms/minute versus the deposition temperature for the chemical vapor deposition using phosphine, ammonia, oxygen and nitrogen carrier gas at a given feed rate of phosphine, 2.12 cc/min. It is seen that the deposition rate peaks at about 500°C deposition temperature. The deposition rate then drops down to the level of somewhat less than 200 Angstroms/min. around 800°C. This deposition rate with respect to deposition temperature can be higher or lower depending on the feed rates of source materials, particularly the phosphine concentration.

The chemical vapor deposited (CVD) phosphorus-nitrogen-oxygen film is a coherent, homogeneous, amorphous material. The processes take place in the deposition. These include, simultaneously, chemical reactions, mass and energy transfers. The overall reaction is as follows:

$$N_2 + PH_3 + NH_3 + O_2 \rightarrow (P_xN_yO_z)_n + P_2O_5 + H_2O + N_2$$

in which $(P_xN_yO_z)_n$ is CVD formed dense material, free of any crystallinity. P_2O_5 and H_2O appear to be the essential reaction by-products along with unidentified trace products in the existing gaseous stream. Microprobe analysis of the film (5000 to 7000 Å thickness) with chemical formula shown above, $(P_xN_yO_z)_n$, indicates X value varying from 30 to 32 atomic percent, y value from 36 to 48 atomic percent and z value from 21 to 33 atomic percent depending on the oxygen concentration in the feed gases mixture as well as deposition temperature.

Preferred composition in terms of wt.% of P-N-O film in the formula $(P_xN_yO_z)_n$ is:

P 48-50 Wt.%
N 29-36 Wt.%
O 10-27 Wt.%

These Wt.% ranges may vary somewhat when deposition temperatures are above or below 650°C.

Figure 6 illustrates the preferred composition region of $(P_xN_yO_z)_n$ at 650°C. Figure 6 gives O, N and P in atomic percent. The Table I gives for Points 4-10 the deposition conditions and O, N and P in the resultant film in weight percent.

TABLE I

Point #	Temp. °C.	O_2% in Gaseous Feed Mixture	Wt.% O	Wt.% N	Wt.% P
4	650	0.015	16.24± 0.49	33.86± 0.37	49.89± 0.30
5	650	0.35	20.93± 1.92	30.52± 0.76	48.54± 1.28
6	650	24	21.32± 0.75	29.58± 0.54	49.09± 0.79
7	650	47.6	21.51± 1.77	29.71± 1.24	48.76± 0.72
8	650	91	26.44± 0.57	25.77± 0.41	47.78± 0.77
9	650	0.35(100 cc/min.) (B_2H_6)	10.06± 1.48	35.50± 0.51	50.42± 1.19
10	800	24 (300 cc/min. (B_2H_6)	16.57± 0.94	35.74± 0.60	47.67± 0.63

Points 1 and 2 represent the compounds PN and P_3N_5, respectively, and Point 3 the simple PON compound. All of these known compounds are prepared by methods other than the CVD process. Points 8 and 9 of Figure 6 represent boron doped $(P_xN_yO_z)_n$ films at 650°C and 800°C. Compositions of the doped films shown in this P-N-O diagram are arrived at by neglecting the boron content because the light boron element is beyond the test probe detection capability. The $(P_xN_yO_z)_n$ film when deposited on a thick silicon wafer with thickness of about 1 micron, exhibits three broad, strong characteristic absorption bands centered at 1230, 910 and 480 cm^{-1}. These bands show very feeble shift with variation of oxygen concentration during deposition.

Referring now to Figure 7, the dielectric constant of the phosphorus-nitrogen-oxygen film varies from 8 to about 6 depending upon the film deposition temperature as shown from this graph. The highest dielectric constant is obtainable at the lower film deposition temperatures. However, the dielectric constant does increase at the higher deposition temperatures of the order of 800-900°C wherein it approaches the higher dielectric constant obtained at the low approximately 400°C film deposition. The minimum film dielectric constant of the material is obtained in the order of 600°C. The graph compares the present material, curve 30, to silicon nitride as deposited 32 and silicon nitride after a 20 hour 1000°C nitrogen annealing 34. Prolonged annealing of Si_3N_4 generally increases the dielectric constant due to an extensive increase of crystallinity of silicon nitride. With the exception of the present material deposited at temperatures below 550°C, this truly amorphous material has comparable dielectric constant to silicon nitride with or without post-deposition anneal.

The refractive index is also dependent upon the deposition temperature as shown by Figure 8. The data points on this graph show experimental points where coatings of the phosphorus-nitrogen-oxygen material were deposited at the various deposition temperatures using the CVD chemical vapor deposition process of phosphine, ammonia, and nitrogen carrier gas. The results show that a steady increase in the refractive index is obtained when moving from the 400°C deposition temperature to the 900°C deposition temperature in the refractive index from about 1.6 to 2.0 as determined at wavelength 5461 Å.

The dielectric constant of the present material is also dependent on oxygen concentration as well as the deposition temperature. Table II illustrates examples of such property dependence.

TABLE II

Deposition Temp.°C	Refractive Index n at 5461Å	Film Thickness in Å	O_2 cc/min	N_2 liter per min.	O_2% in Feed	Dielectric Constant
860	1.89	1046	5000	15.5	24.4	6.95
800	1.942	960	10	20.5	0.05	7.49
800	1.931	813	8	20.5	0.039	6.8
550	1.711	1130	4	10.5	0.038	6.3
550	1.722	1151	2	10.5	0.019	6.3
500	1.717	1169	2	8.8	0.0235	6.2
450	1.682	1189	2	7.5	0.0266	6.74
655	1.876	1000	2	12.5	0.016	6.8
850	1.961	882	8	20.5	0.039	7.08
610	1.772	863	2	12.5	0.016	6.58
800	1.857	1229	5000	15.5	24.4	6.54
650	1.747	1299	5000	5.5	47.6	6.7
700	1.931	922.7	2	16.5	0.012	6.75

The Table III indicates the dielectric breakdown strength (accumulation mode) for the phosphorus-nitrogen-oxygen coatings deposited on the bare silicon substrates using phosphine, ammonia, oxygen and nitrogen carrier gas.

TABLE III

Deposition Temp.°C	Breakdown Strength, $X10^6$ V/cm
500	13.8
600	14.7
700	12.8
800	84
860	10

The dielectric breakdown strength of Table III was measured by the ramp method on 20 mil diameter aluminum dot over the P-N-O film of approximately 1000 Å on N type (100) Si substrates. For comparison purpose, all the breakdown strength was calculated based on equivalent silicon dioxide thickness. As compared to Si_3N_4 films deposited on Si substrates in the same temperature range, the breakdown strength of P-N-O film is two to three times better than that of silicon nitride. In comparison with Si_3N_4, P-N-O coating not only shows higher dielectric breakdown strength, but also exhibits better compatibility to silicon substrate. Films of the P-N-O coating up to 2 microns in thickness on silicon do not cause any stress cracking or substrate warpage. Si_3N_4 on silicon substrate generally shows cracks and warpage when its thickness reaches 0.8 microns.

The phosphorus-nitrogen-oxygen material is very stable and does not decompose at normal temperatures in the range of 900°C. The material is not attacked by water, sulphuric acid, hydrochloric acid, hydrofluoric acid, phosphoric acid, ammonium hydroxide, hydrogen peroxide, ammonium hydroxide plus hydrogen peroxide, hydrogen peroxide plus hydrochloric acid, nitric acid, hydrofluoric acid plus nitric acid, aqua regia, sodium hydroxide solution (about 50%), pyrocatechol-ethylemediamine-water system. It is not even wetted by hydrofluoric acid solution.

The stability of the material is such it is difficult to etch using normal chemical etching techniques. Reactive ion etching may be satisfactorily accomplished using a carbon tetrachloride system. For example, in carbon tetrachloride reactive ion etching at a temperature of 225°C will etch the phosphorus-nitrogen-oxygen material at about 30 Angstroms per second.

The P-N-O material is virtually not attacked by concentrated sulfuric acid (H_2SO_4) at temperatures below 100°C. The material, however, can be chemically etched only with concentrated H_2SO_4 at elevated temperatures. Figure 9 shows the etch rate of the material using 96% H_2SO_4 at temperatures from 100°C to 230°C. For pattern definition, the P-N-O film is CVD coated with approximately 1000 Å SiO_2, then processed with conventional photolithography etching off unwanted oxide area. High temperature concentrated H_2SO_4 etch will remove the P-N-O film through the opened oxide window. The preferred etching temperature using H_2SO_4 is above about 190°C and below the boiling or fuming point of H_2SO_4.

There are many applications where this phosphorus-nitrogen-oxygen amorphous material because of its excellent stability and ability to withstand chemical attack. One important application would be as a diffusion source for phosphorus into silicon wafers. This diffusion would produce an N type region in silicon which is important in the manufacture of transistors and integrated circuits. High levels of phosphorus concentration in the diffused region can be produced from the present coating of in the order of 10^{20} to 10^{21} atoms per cc. and the junction depth of 1.2 to 1.4 microns. Diffusion was carried out at 1000°C or higher in O_2 ambient. P-N-O film deposited on Si wafers of 0.5 to 1 microns in thickness was positioned in about 0.030″ away from the device to be diffused. The time at temp. is about 1/2 to 1 hour with O_2 at 1 litre/min. flowing through the reaction tube.

Another important application is the use of the P-N-O film in FET memory devices in the gate region. The structure would be, for example:

(1) Metal/P-N-O film/silicon device (MPS).
(2) Metal/P-N-O film/SiO_2 silicon device (MPOS).
(3) Silicon/P-N-O film/SiO_2/silicon device (SPOS).

Table IV gives experimental data on MPOS [Al metal-$(P_xN_yO_z)_n$-SiO_2-Si] device where a 20 mil diameter Al dot on $(P_xN_yO_z)_n$ over 200 Å SiO_2 on P(100) Si substrate.

TABLE IV

Temp.°C	O_2%	Equivalent Oxide Å	V_{FB}	Net Charge per cm^2
800	0.034	289	−1.20V	2.87×10^{11}
850	0.034	268	−1.10V	2.32×10^{11}
700	0.014	291	−1.20V	2.85×10^{11}
600	0.016	323	−1.12V	2.06×10^{11}
500	0.024	320	−0.99V	1.23×10^{11}
450	0.026	310	−0.96V	1.07×10^{11}

Other applications include wire insulation, capacitor, protective coating for integrated circuits or other uses, an etching mask.

The following examples are included merely to aid in the understanding of the invention.

Example 1

Silicon substrates were placed on the graphite susceptor of the horizontal reactor shown in Figure 1. The reactor was 3 1/4" by 2 1/4" and 30" long. The induction heating was turned on and the temperature of the silicon substrates was raised to between 400 and 900°C depending upon the particular experiment within this example. Constant gaseous feed rates of phosphine PH_3 was 2.1 cc/min. and ammonia NH_3 was 200 cc/min. The oxygen content in the nitrogen carrier gas was varied. The oxygen was varying from 1 to 5000 cc/min. and N_2 from 3 litres/min. to 20.5 litres/min. depending on the deposition temperature. In Figure 4, the lowest amount of O_2 in the feed is one cc/min. and the highest 5000 cc/min. The maximum N_2in the feed mixture is 20.5 litres/min. At each deposition temperature there is a favourable total feed rate so that the most uniform film thickness can be produced. The total flow rate generally increases with deposition temperature. Films in Figure 4 have thickness varying from approximately 1000 Å to a few microns. The crosses and squares on Figure 4 are actual data points of deposition temperature in °C versus oxygen concentration in feed gaseous mixture excluding ammonia and phosphine. It is seen from the Figure 4 that the phosphorus-nitrogen-oxygen material is only successfully formed within the dashed line. Outside of this dashed line either no deposition occurred or unstable coating occurred.

Example 2

A silicon wafer having the phosphorus-nitrogen-oxygen coating prepared by the method embodying the invention as disclosed in Example 1 was subjected to boiling water at the deposition temperatures of 470°, 500° and 700°C. The coating was not affected after 7 days of continuous subjection to boiling water.

Example 3

Phosphorus-nitrogen-oxygen coating prepared by the method embodying the invention as disclosed in Example 1 at temperatures above 450°C was not affected after 12 days of continuous subjection to room temperature water.

Example 4

Silicon wafers having phosphorus-nitrogen-oxygen coatings thereon were formed at the film deposition temperatures specified in the Table V in accordance with the method embodying the invention as disclosed in Example 1. The wafers were subjected to a temperature of 1000°C in O_2 for one hour. The coatings disappeared. The wafers were then cleaned with HF and rinsed in H_2O. The diffusion results showed a shallow junction of 0.18 to 0.29 microns, surface concentration in the order of 10^{19} atoms/cm^3 and sheet resistance from 300 to 1000 ohm/square. The data showed no dependence of film deposition temperature.

TABLE V

	Film Deposition Temp.°C.	Junction Depth,Microns	Surface Concentrations in atoms/cm^3	Sheet Resistance ohm/square
4A	400	0.29	$10^{19.2}$	240
4B	450	0.19	$10^{18.7}$	1003
4C	650	0.18	$10^{18.5}$	951
4D	750	0.21	$10^{19.2}$	418
4E	900	0.25	$10^{19.2}$	309

WHAT WE CLAIM IS:-

1. A method of forming an amorphous phosphorus-nitrogen-oxygen film comprising providing a reaction chamber with a substrate disposed therein, said chamber having a substrate temperature from 400° to 900°C, passing reaction gases PH_3, NH_3 and a gas which is a source of oxygen through the chamber to deposit onto said substrate a film of phosphorus-nitrogen-oxygen material having a formula $(P_x N_y O_z)_n$ wherein x is from 30 to 32 atomic percent, Y is from 36 to 48 atomic percent and z is from 21 to 33 atomic percent.

2. A method according to claim 1, wherein said gas is O_2.

3. A method according to claim 1 or 2, wherein the reaction chamber has a substrate temperature of 450° to 850°C.

4. A method according to any one of claims 1 to 3, wherein oxygen is greater than 0.01% of the reaction gas mixture.

5. A method according to any one of the preceding claims, wherein gas feed rates into said chamber are between 0.5 and 2.5 cc/min. for PH_3 and between 100 cc/min. and 300 cc/min. for NH_3.

6. A method according to any one of the preceding claims, wherein an inert carrier gas is used and its feed rate is between 3 litres/min. and 20.5 litres/min.

7. A method according to claim 6, wherein said inert carrier gas is N_2.

8. A method according to any one of the preceding claims, wherein a source of boron is included in the reaction gases to dope said film with boron.

9. A substrate having a coating of amorphous phosphorus-nitrogen-oxygen material having a formula $(P_x N_y O_z)_n$, wherein x is from 30 to 32 atomic percent, y is from 36 to 48 atomic percent and z is from 21 to 33 atomic percent.

10. A substrate according to claim 9, wherein the refractive index of said material is between 1.6 and 2.0 measured at wavelength 5461 Å.

11. A substrate according to claim 9 or 10, wherein the dielectric constant of said material is between 6 and 9.

12. A substrate according to any one of claims 9 to 11, wherein the dielectric breakdown strength of said material on bare silicon is between 10 to 20 × 10^6 volts/cm based on equivalent oxide thickness.

13. A substrate according to any one of claims 9 to 12, wherein said material includes 48-50 percent by weight of phosphorus, 29-36 percent by weight of nitrogen and 10-27 percent by weight of oxygen.

14. A method of forming phosphorus-nitrogen-oxygen film according to claim 1 substantially as hereinbefore described.

15. A substrate made by the method claimed in any one of claims 1 to 8 and 14.

16. A semiconductor electronic structure comprising a silicon body having semiconductor devices therein and a coating of amorphous phosphorus-nitrogen-oxygen material over at least a portion of one surface thereof, said material having a formula $(P_x N_y O_z)_n$, wherein x is from 30 to 32 atomic percent, y is from 36 to 48 atomic percent and z is from 21 to 33 atomic percent.

17. A semiconductor structure according to claim 16, wherein a layer of silicon dioxide

is located between said silicon body and coating.

18. A semiconductor structure according to claims 16 or 17 comprising a metal film coated over said phosphorus-nitrogen-oxygen coating.

19. A semiconductor structure according to claim 18, wherein said structure is a field effect transistor, said metal film its gate electrode and said coating the gate dielectric.

20. A semiconductor structure according to claim 19, wherein said gate dielectric also includes a silicon dioxide coating.

21. A semiconductor structure according to any one of claims 18 to 20, wherein said metal film is polycrystalline silicon or aluminium.

22. A semiconductor structure according to claim 16 substantially as hereinbefore described.

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Agent for the Applicants.

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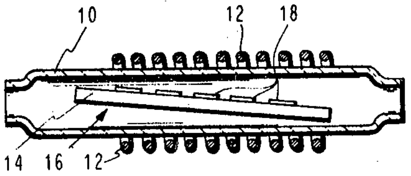

FIG. 1

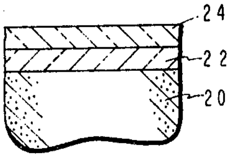

FIG. 2

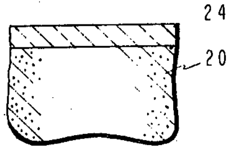

FIG. 3

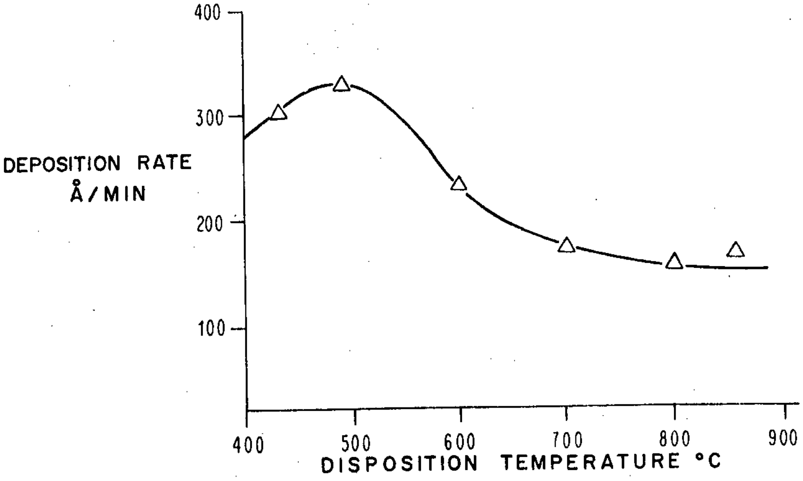

FIG. 5

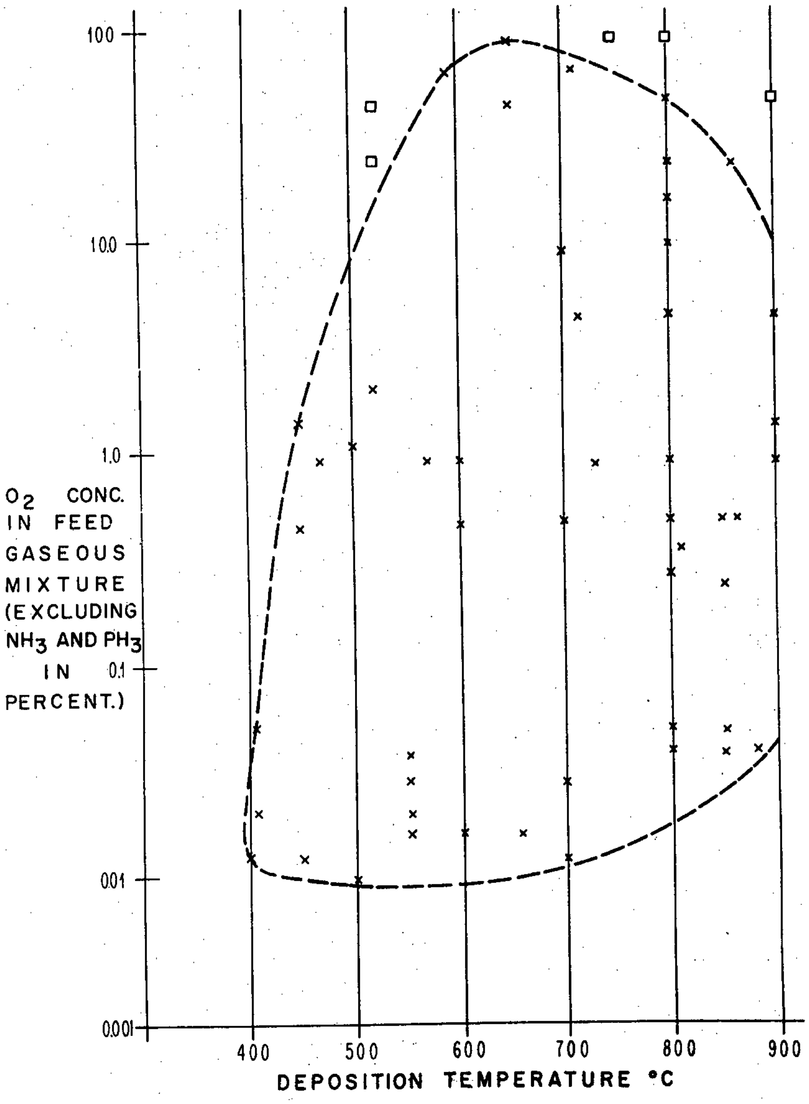
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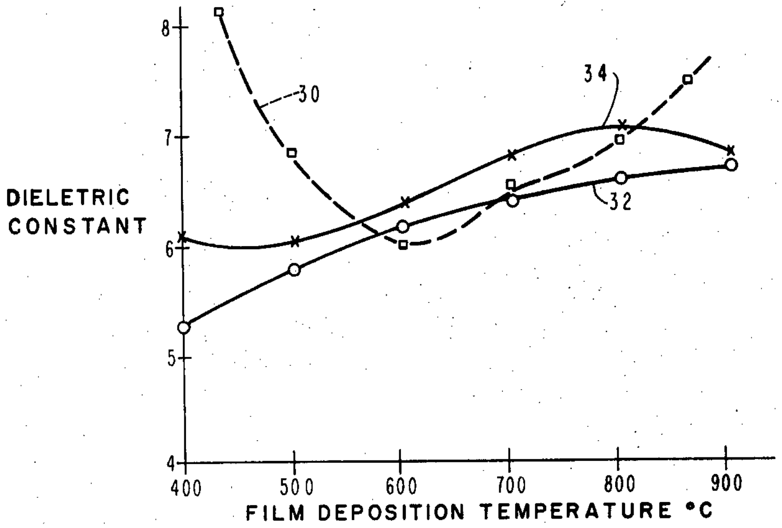
FIG. 4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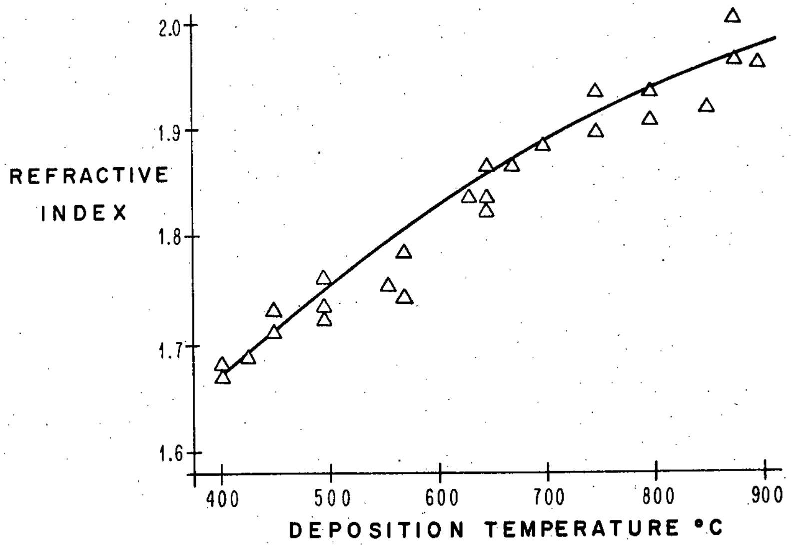
FILM DEPOSITION TEMPERATURE °C

FIG. 7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DEPOSITION TEMPERATURE °C

FIG. 8

FIG. 6

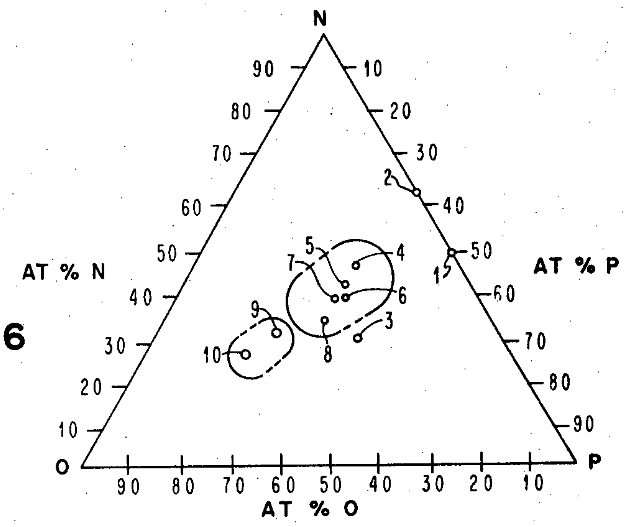
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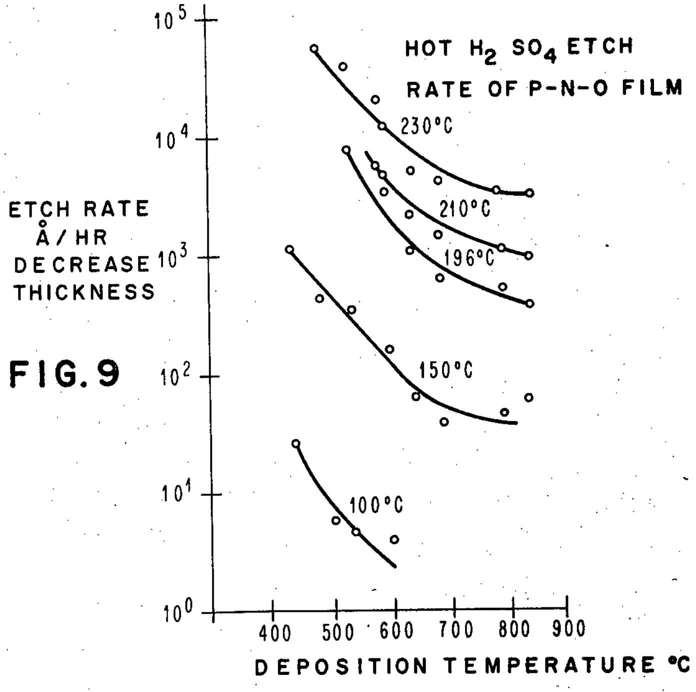
FIG. 9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800
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DEPOSITION TEMPERATURE °C