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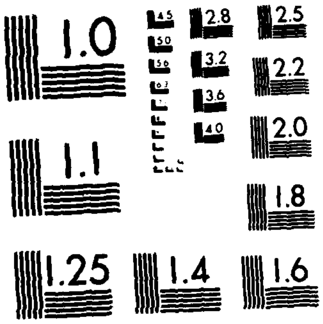

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FINAL REPORT

Contract No. N00014-84-K-0459

Office of Naval Research (Mr. Max N. Yoder, Electronic Division)
800 North Quincy Street
Arlington, Virginia 22217

Interfacial Properties of Germanium Nitride Dielectric Layers on Germanium

30 Sep 1986

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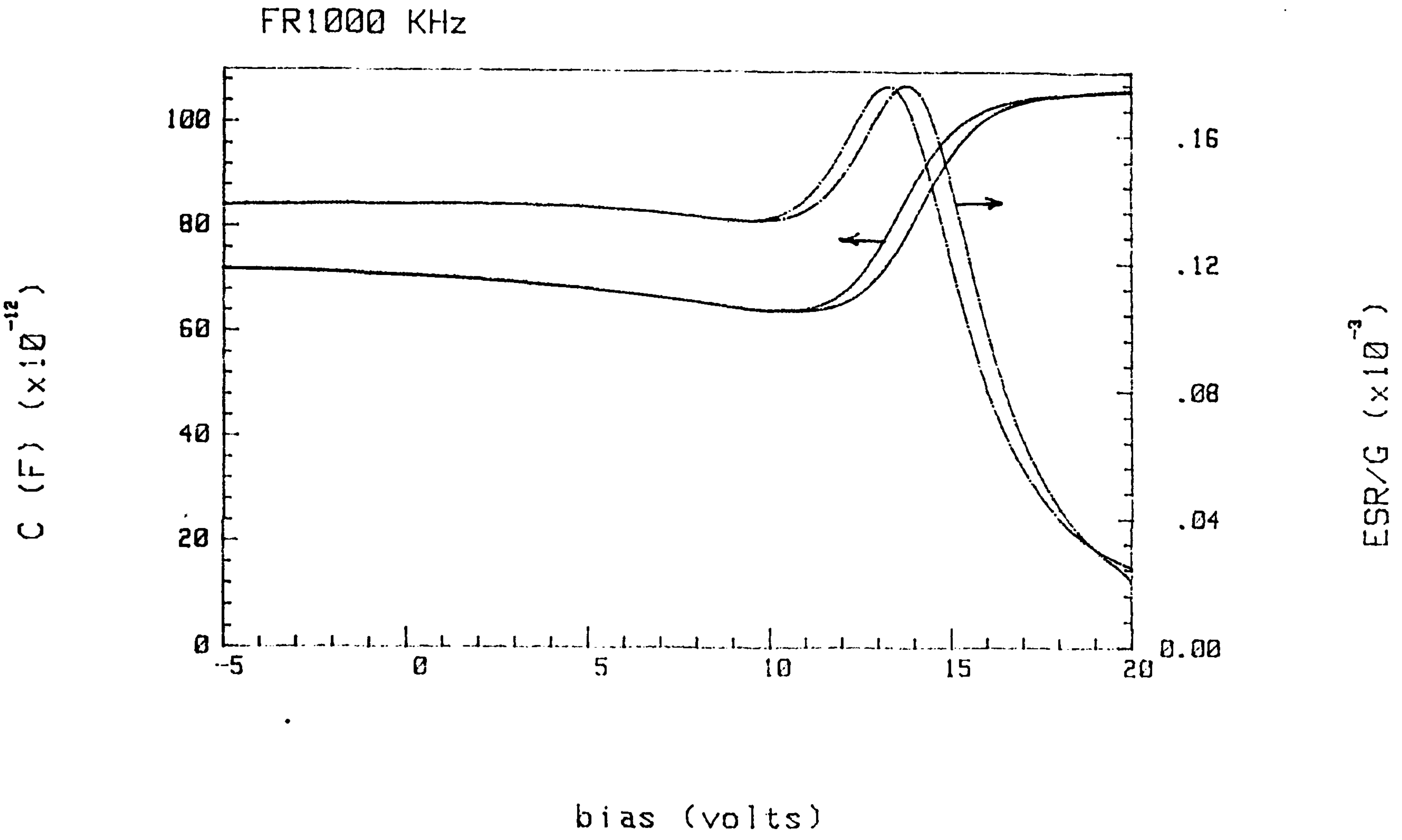
Abstract

The enclosed report represents work performed at UCSD on Contract N00014-84-K-0459 entitled, "Interfacial Properties of Germanium Nitride Dielectric Layers on Germanium", and provides a full account of the results obtained during the contract period: July 1, 1985 to September 30, 1986. The paper, "Growth of Amorphous Germanium Nitride Films by Indirect Plasma CVD", has been published in the JOURNAL OF THE ELECTROCHEMICAL SOCIETY, Volume 134, page 979 (1987). The remainder of this report describes additional unpublished results.

The second year's effort on this project has been focused on optimizing the quality of germanium nitride layers on germanium substrates and optimizing the interfacial properties of these structures. The electrical and physical properties of these layers have been reported in the attached article. One of the most difficult problems we encountered was that while the Ge_3N_4 layers gave improved interfacial properties on the Ge substrates, we could never get the resistivity of our deposited Ge_3N_4 above about $10^{14}\Omega$ cm. This gave us larger hysteresis in the C-V curves than we would like to have seen and made low frequency C-V measurements difficult. This difficulty is often not stated explicitly in other published work on this material, but if you read between the lines it seems other workers have had similar problems. We have tried various annealing treatments in O_2, N_2 and H_2 before and after the Ge_3N_4 deposition and have not seen improvements in the electrical properties of the MIS capacitors which were impressive.

The reported bandgap of Ge_3N_4 is somewhat low (4.7 eV). We wondered if reductions in the DC leakage currents through the deposited layers could be achieved if Si were reacted with ammonia to form Si_3N_4 layers since the bandgap of Si_3N_4 (5.3 eV) is somewhat larger than for Ge_3N_4, and it is known that highly insulating layers of Si_3N_4 may be fabricated. The problem with depositing Si_3N_4 directly on Ge is well illustrated by Fig. 1 which shows the 15 V flatband shift which occurs when this dielectric is deposited directly on a Ge substrate. We have constructed double layer $Si_3N_4/Ge_3N_4/Ge$ and $Si_3N_4/Si_xGe_yN/Ge$ capacitors and have achieved the best results using the $Si_3N_4/Si_xGe_yN/Ge$ structures. Representative C-V data for these devices are shown in Figs. 2 and 3. The 0.4 V hysteresis for the device in Fig. 3 is the smallest we have seen for any processing technique we have tried on germanium.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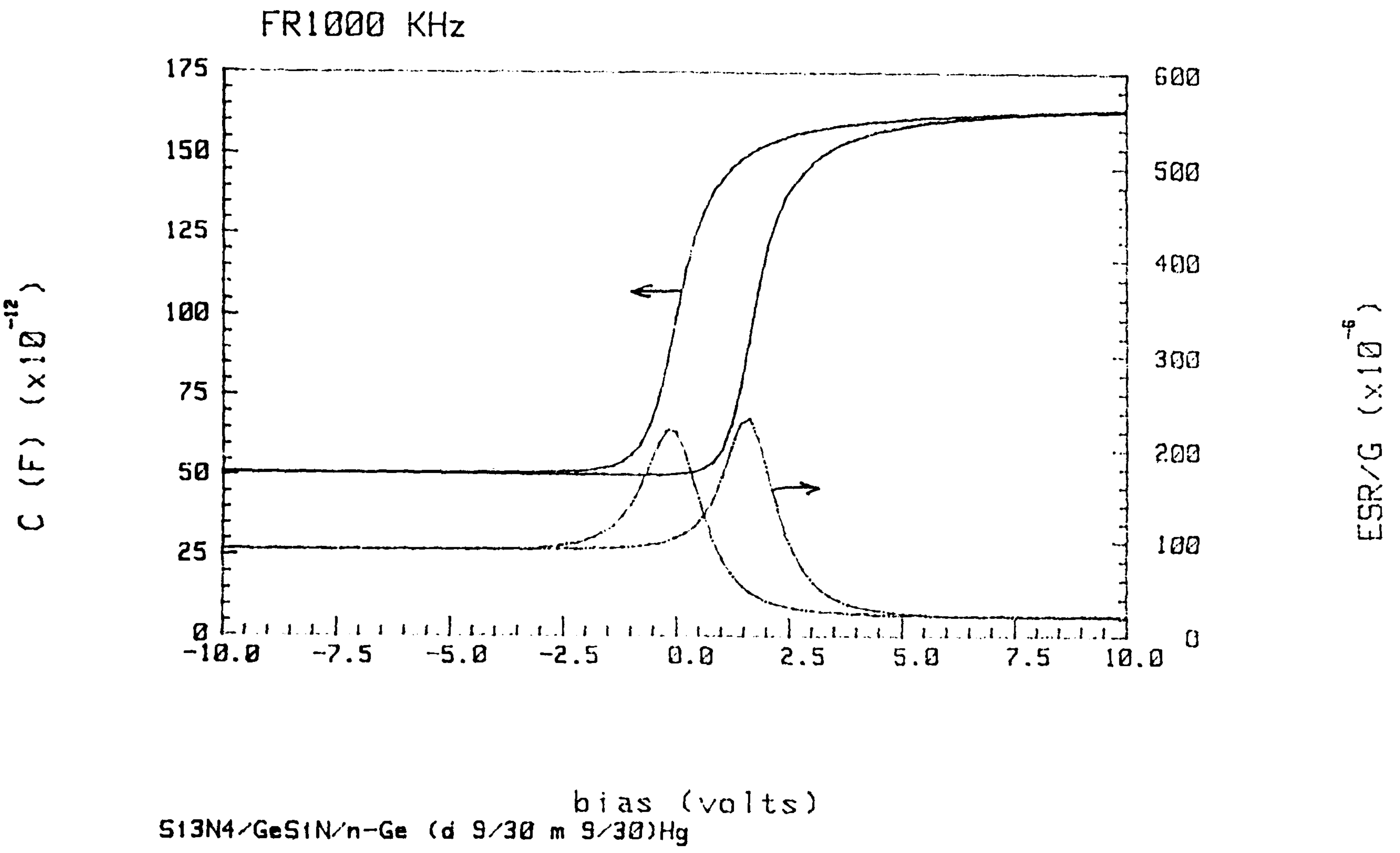
C (F) (x10^{-12})
100
80
60
40
20
0
ESR/G (x10^{-3})
.16
.12
.08
.04
0.00
-5
0
5
10
15
20
bias (volts)

Fig. 1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150
125
100
75
50
25
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C (F) (x10^-12)
600
500
400
300
200
100
0
ESR/G (x10^-6)
-10.0
-7.5
-5.0
-2.5
0.0
2.5
5.0
7.5
10.0
bias (volts)
SI3N4/GeSIN/n-Ge (d 9/30 m 9/30)Hg

Fig. 2

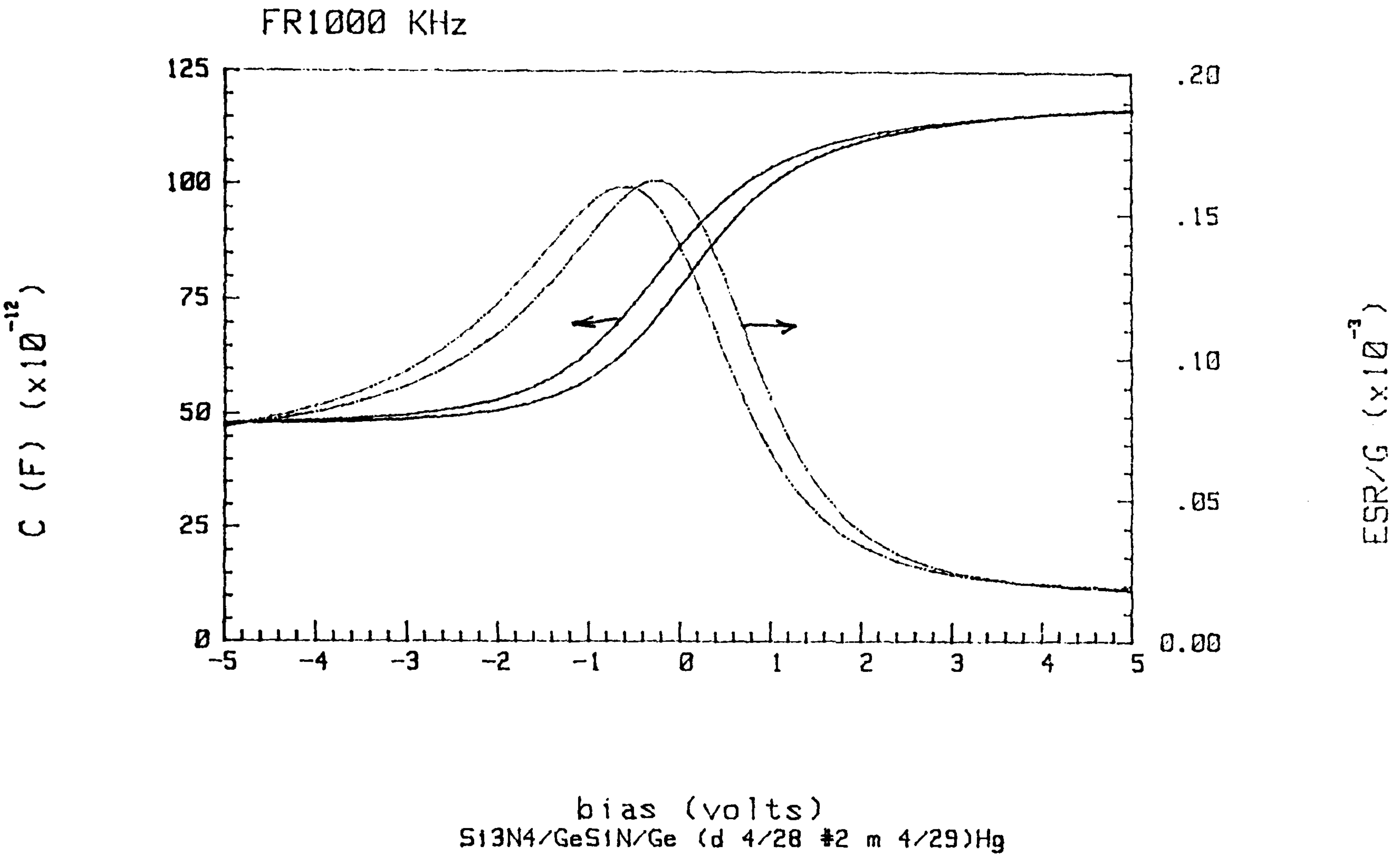
FR1000 KHz
125
100
75
50
25
0
C (F) (x10^-12)
.20
.15
.10
.05
0.00
ESR/G (x10^-3)
-5
-4
-3
-2
-1
0
1
2
3
4
5
bias (volts)
S13N4/GeSIN/Ge (d 4/28 #2 m 4/29)Hg

Fig. 3

Growth of Amorphous Germanium Nitride Films by Indirect-Plasma Enhanced CVD

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ABSTRACT

Growth of Ge_3N_4 films was achieved by microwave-sustained indirect-plasma enhanced chemical vapor deposition (CVD) using GeH_4 and NH_3 as the source gases. Layers were deposited on single crystal substrates of Ge and Si and capacitance-voltage (C-V), infrared absorption, and ellipsometric measurements were performed. Films grown at 300°-400°C were primarily α-Ge_3N_4. High frequency (1 MHz) C-V measurements exhibited approximately 2V hysteresis and a fast interface state density estimated to be less than 5×10^{11} cm^{-2} eV^{-1}.

Development of a high speed complementary FET technology based on germanium MIS structures would be possible if a dielectric film could be grown such that a stable, device quality, dielectric-semiconductor interface could be formed. The development of a technology for forming such interfaces has been hindered by the fact that the native oxides formed on germanium are rather unstable. The monoxide sublimes at 710°C. This makes it very difficult to grow the dioxide thermally since the formation and subsequent sublimation of the monoxide provides a reaction path for the transport of germanium away from the surface and leads to the creation of voids underneath the growing dioxide layer (1). The growth proceeds uniformly only after enough GeO_2 has formed to act as a cap to prevent the sublimation of GeO. The GeO_2 layers once formed are not readily amenable to further chemical processing. Two crystalline forms of GeO_2 have been reported: a hexagonal and a tetrahedral structure. The hexagonal structure is soluble in aqueous solution which is consistent with the fact that thermally grown films can usually be washed off in water. In an effort to create a more stable dielectric layer on germanium, a number of workers have employed various deposited layers on germanium. While this provides a chemically stable interface, the interface state densities that are observed on such structures are usually quite high. The initial work on deposited dielectrics on germanium was confined to the CVD oxides SiO_2 and Al_2O_3 (2-5). The electrical properties of the MIS structures formed with these dielectrics were characterized by rather large densities of both fast and slow states at the interface between the insulator and the semiconductor. Due to the large density of fast interface states present in these structures analysis of C-V data was not possible unless high frequency (>10 MHz) or low temperature (77 K) was employed to increase the charging time constants of the fast states, relative to the measurement frequency, so that the surface-state capacitance was negligible (2). At room temperature n-type samples tended to have a surface which was near flatband or slightly depleted, and the surface-state density was too high to induce inversion at room temperature with a gate voltage below that which produces dielectric breakdown (3). At 77 K the time constants of the surface states were increased, and the Fermi level at the surface could be modulated over the entire bandgap, but it was not clear that an inversion layer was actually being formed. Presumably the poor electrical behavior of the SiO_2 and Al_2O_3 layers on germanium is due to the fact that the oxygen, which is present as part of the SiO_2 CVD deposition process, creates under the deposition conditions an underlayer of native oxide of a type which serves as a medium for the trapping of charge.

Much improved interfacial electrical properties have been obtained on germanium by substituting Ge_3N_4 for SiO_2 as the dielectric. A strikingly different feature of the electrical measurements on such layers is the reduction of the number of interface states and the increase of their time constants. The previously reported work on the deposition of Ge_3N_4 layers on germanium employed $GeCl_4$ and NH_3 as the reactant gases. Although NH_4Cl is an undesirable by-product of this reaction, it sublimes at 335°C and should not become incorporated into the layers if the substrate is kept above this temperature. A potentially more disturbing problem associated with the use of $GeCl_4$ is the incorporation of chlorine into the deposited layers. Comparison studies have been made using both SiH_4 and $SiCl_4$ as source materials for the growth of SiO_2 and Si_3N_4 layers in the same plasma CVD reactor. Invariably the layers grown using $SiCl_4$ had electrical properties (low breakdown voltage and high interface state density) which were inferior to those of layers grown using SiH_4 (6). In the case of the SiO_2 layers grown using $SiCl_4$ the results were very similar to reported results on Cl-doped thermally grown SiO_2 layers in which too much Cl_2 or HCl is present in the reactor during oxide growth. In light of those results it is tempting to speculate that the $GeCl_4$-NH_3 reaction would not be the first choice for a process for growing Ge_3N_4 layers on germanium.

This paper reports growth of amorphous germanium nitride films by microwave-sustained indirect-plasma enhanced CVD from the reaction of germane (GeH_4) and ammonia (NH_3) on substrates of single crystal Ge or Si. The constraints imposed by the low decomposition temperature of GeH_4 are discussed.

Experimental

Growth of the films was accomplished in a horizontal quartz tube enclosed by a split tube resistance heated furnace. As shown in Fig. 1, a plasma was generated in an adjacent chamber by passing NH_3 gas through a coaxial microwave resonant cavity excited in the TE_{011}* hybrid mode at 2.45 GHz equipped to supply 0-600W power. The afterglow of this plasma was carried into the deposition chamber through a 5 mm id quartz tube and directed onto the substrate. GeH_4 supplied as 10% in N_2 was additionally diluted with N_2 and entered the reaction vessel separately. The high purity NH_3 gas was bubbled through a gallium-indium eutectic alloy containing dissolved aluminum metal, to scavenge water vapor and oxygen which might be present as impurities in the NH_3 (7).

The layers were deposited on single crystal $n = 3 \times 10^{15}$ cm^{-3}, (100) oriented-Ge and on $n = 1 \times 10^{15}$ cm^{-3},

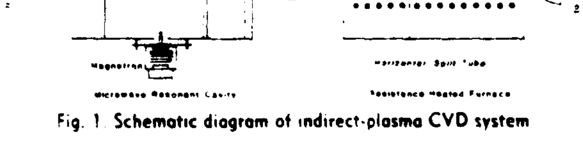

Fig. 1. Schematic diagram of indirect-plasma CVD system

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* Electrochemical Society Active Member

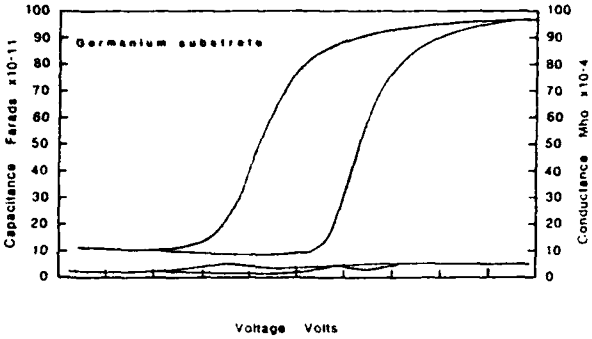

Fig. 2. Capacitance vs. voltage and conductance vs. voltage measurements on an Al-Ge_3N_4-Ge MIS device.

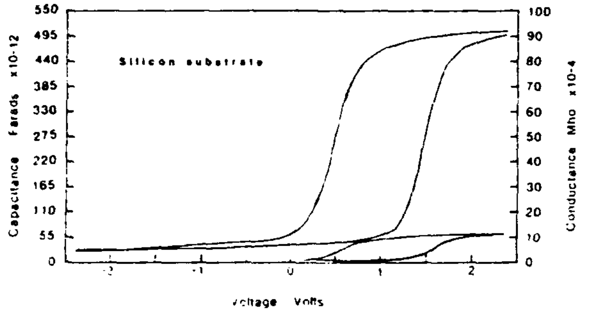

Fig. 3. Capacitance vs. voltage and conductance vs. voltage measurements on an Al-Ge_3N_4-Si MIS device.

(100)-oriented silicon substrates. Immediately prior to deposition the substrates were etched in HF and rinsed in DI water. The substrates were raised to deposition temperature in an N_2 ambient, the NH_3 and the GeH_4 were subsequently turned on and the deposition began when power was applied to the microwave cavity.

Results

Growth of Ge_3N_4 films by IPECVD was accomplished in the temperature range of 300°-400°C at pressures of about 1.4 torr and deposition times of about 15 min. The maximum growth temperature was limited to approximately 450°C since GeH_4 begins to pyrolytically decompose at about 500°C. When this happens Ge-rich layers result. The growth rate was comparatively insensitive to the power level of the microwave, the NH_3 flow rate, or the pressure. The substrate temperature and GeH_4 concentration determined the film quality and growth rate. Substrate temperatures much below 300°C yielded low growth rates and low refractive index (n = 1.74) films with poor electrical characteristics. A too high GeH_4 concentration resulted in Ge-rich, discolored films, while a too low concentration gave very low growth rates. C-V curves from representative samples grown at 325° and 350°C with flow rates of 130 sccm NH_3, 15 sccm GeH_4 (10% in N_2) mixed with 25 sccm N_2 are presented in Fig. 2 and 3. The deposition rate under these conditions was 4 nm/min.

The thickness and refractive index of the films were determined from ellipsometric measurements at 6328Å (HeNe). Typically the films were about 40 nm thick with refractive indexes varying from n = 1.74 to 2.15. The resistivity varied directly as the refractive index, being lower for low index films. The composition of the films was investigated by measuring the infrared absorption (IR) spectra of layers deposited on silicon substrates. The IR spectrum of crystalline Ge_3N_4 formed by reacting

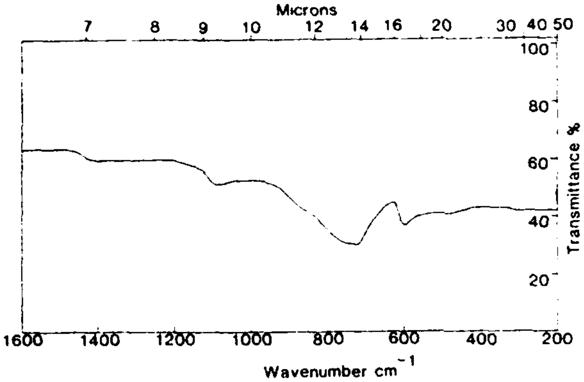

Fig. 4. Infrared transmittance measurements of a Ge_3N_4 layer

Ge with NH_3 above 700°C shows absorption peaks at 770 and 730 cm^{-1}, the latter corresponding to adsorption by α phase Ge_3N_4 (8). The IR plot of one of our layers as shown in Fig. 4, has a broad absorption peak in this wavelength region similar to the data of Nagai and Nimi (8) and which they identify as α-Ge_3N_4. The smaller absorption peaks at 1200 and 600 cm^{-1} are due to traces of SiO_2 on the Si substrate. There is no peak at either 800 or 570 cm^{-1} corresponding to GeO_2, and thus no evidence for oxygen incorporation in the film.

Capacitance-voltage measurements of these layers were made in a light-tight enclosure at room temperature using a 1 MHz bridge at a bias sweep rate of 0.1 V/s. Measurements on representative samples, as shown in Fig. 2 and 3, are dominated by a density of slow traps which gives approximately 2V hysteresis in the negative-going and positive-going curves. The density of fast interface states seems to be low which may be due to the successful removal of oxygen-containing contaminants from the NH_3 gas. The observed hysteresis of about 2V compares favorably with that reported by Yashiro (9) for Ge_3N_4 CVD deposited from pyrolysis of $GeCl_4$ and NH_3 at 450°C.

The saturation of the capacitance at both positive and negative voltages suggests that the surface can be modulated all the way from accumulation to inversion.

Conclusion

The major problem yet to be solved using this method of film growth is the undesirably low bulk resistance of the layer — typically 10^{12}-10^{14}Ω cm. It is thought that the leakage that is presently observed is probably also related to the slow trapping behavior that is present. The leakage is most probably due to nonstoichiometric regions in the deposited layers. A perennial problem with this type of film growth is obtaining a reactor design which will force the reaction of (in this case) GeH_4 to completion once the decomposition of a molecule has been initiated by an excited nitrogen monomer.

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REFERENCES

1. J. T. Law and P. S. Meigs, *This Journal*, **104**, 154 (1957).
2. T. O. Sedgwick, *J. Appl. Phys.*, **39**, 5066 (1968).
3. T. Yashiro, *Jpn. J. Appl. Phys.*, **9**, 740 (1970).
4. K. L. Wang and P. V. Gray *This Journal*, **123**, 1392 (1976).
5. S. Iwanchi and T. Tanaka, *Jpn. J. Appl. Phys.*, **10**, 260 (1971).
6. L. G. Meiners, Unpublished data.
7. J. R. Shealy and J. M. Woodall, *Appl. Phys. Lett.*, **41**, 88 (1982).
8. H. Nagai and T. Niimi, *This Journal*, **115**, 671 (1968).
9. T. Yashiro, *ibid.*, **119**, 780 (1972).

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