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GaAs SURFACE PASSIVATION FOR DEVICE APPLICATIONS

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Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, CA 90265

December 1980

Interim Report for period 15 December 1979 through 14 June 1980

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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This report describes the progress in the fourth six-month period of a program to develop deposited dielectrics for GaAs device applications. Three applications of the dielectrics are being investigated: (1) isolation of control electrodes, (2) passivation of the GaAs surface, and (3) encapsulation of completed circuits. The dielectrics being studied include silicon oxynitride; mixtures of silicon nitride

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and germanium nitride; and mixtures of silicon dioxide, gallium oxide, and aluminum oxide. During this reporting period, studies of the interface properties of pyrolytically deposited Si_3N_4 on n-type GaAs under illuminated conditions were performed. The data obtained are consistent with the interpretation that inversion of the GaAs surface is being achieved. In addition, process parameters for plasma-enhanced deposition of silicon nitride films with low oxygen content and refractive index near that of stoichiometric Si_3N_4 were determined. Evaluation of the interface properties of SiO_2 films deposited on GaAs by photochemical deposition is also reported.

PREFACE

The work reported here is supported by the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, under contract F33615-78-C-1444, Project Number 2305, Task Number 2305R1. The monitoring engineer is Capt. R.L. Johnson (AFWAL/AADR). The program objective is to investigate the passivation of gallium arsenide and the application of dielectric thin-film overlayers in metal-insulator-semiconductor field-effect transistors.

This work is being performed jointly by Hughes Research Laboratories Malibu, CA 90265 and the Technology Support Division of Hughes Aircraft Company, Culver City, CA 90230. Contributions to this work have been made by C.L. Anderson, M.D. Clark, A.J. Mohr, J.W. Peters, R.A. Jullens, and F.L. Gebhart.

This is the fourth interim report. The first, second, and third were published as AFAL-TR-79-1057, AFAL-TR-79-1234, and AFWAL-TR-80-1149, respectively, with the same title. This report covers the period 15 December 1979 through 14 June 1980. The submittal date of this report was December 1980.

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INTRODUCTION AND SUMMARY

The goal of this program is to develop dielectrics that will serve the following three basic purposes in gallium arsenide device technology:

- Passivation — reduction of the number of electrically active centers ("surface states") at the semiconductor surface so that the surface potential can be modulated by control electrodes ("gates") overlying the dielectric.
- Isolation — insulation of control electrodes from each other and from the substrate.
- Encapsulation — overcoating of operational circuits to reduce their sensitivity to environmental influences.

To serve these three purposes, Hughes Aircraft Company is developing a variety of deposited dielectrics. Techniques for depositing these dielectric materials are being developed under Hughes internal funding. Evaluation and optimization of these materials for GaAs device applications are being performed under the subject contract.

The following materials are being developed:

- $Ga_xAl_yO_z$ (gallium-aluminum oxide), referred to as (Ga, Al)O
- $Ga_xSi_yO_z$ (gallium-silicon oxide), or (Ga,Si)O
- $Al_xSi_yO_z$ (aluminum-silicon oxide), or (Al,Si)O
- SiO_xN_y (silicon oxynitride)
- (Si,Ge)N (silicon-germanium nitride).

Three basic techniques for depositing these materials are being evaluated:

- Pyrolytic chemical vapor deposition (CVD)
- Plasma-enhanced deposition (PED)
- Photochemical deposition (PCD).

We reported in AFAL-TR-79-1057 the successful use of our proprietary plasma-deposited glass as an isolation dielectric in GaAs MESFET ICs. In AFAL-TR-79-1234, we reported the application of this dielectric as an encapsulant for discrete GaAs MESFETs with the loss of only 0.5 dB gain at 9.7 GHz. Because of the demonstrated utility of this dielectric for isolation and encapsulation applications, this program has been redirected to investigate the application of deposited dielectrics solely for passivation applications.

In the previous report (third interim report for this contract, AFWAL-TR-80-1149), we described a process for depositing pyrolytic Si_3N_4 on GaAs at 615°C. Capacitance-voltage (C-V) data on these films exhibited moderate frequency dispersion in the accumulative regime and the ability to achieve deep depletion. During this reporting period, we have studied the behavior of these films under illuminated conditions. Under these conditions, substantial concentrations of electron-hole pairs are generated near the capacitor structures. The C-V and conductance-voltage (G-V) characteristics of the Si_3N_4 films under these conditions are consistent with the interpretation that inversion is being achieved. These data are presented and discussed in Section 2.

The results presented in AFAL-TR-79-1057 and AFAL-TR-79-1234 clearly indicated that the vacuum technology employed in our commercial plasma reactor (LFE Corp. model PND-301) was inadequate for the fabrication of PED "Si_3N_4" and "Ge_3N_4" with acceptably low oxygen content for passivation applications. The MIS C-V characteristics presented in AFAL-TR-79-1234 strongly suggest that high oxygen content in the deposited films is correlated with poor interface properties, especially "pseudo-inversion." (Pseudo-inversion is the saturation of the capacitance of MIS diodes at values in excess of the theoretical high-frequency inversion capacitance.)

Accordingly, we designed a PED system with improved vacuum technology and fixturing that deposits films with excellent thickness uniformity and composition control. This system, which can deposit films simultaneously on four 5-cm-diameter wafers, is described in AFAL-TR-79-1234. Mechanical assembly of the system was completed durin the third semester of this program. During this semester (the fourth), the system was brought on line. Following some modifications to improve process control, the system was shown to be capable of depositing PED silicon nitride films with low oxygen content and an index of refraction near that expected for stoichiometric Si_3N_4. These results are discussed in Section 3.

During this semester, we also investigated the C-V and G-V behavior of SiO_2 films deposited on GaAs by photochemical deposition (PCD).

SECTION 2

EVALUATION OF PYROLYTIC SILICON NITRIDE FOR GaAs PASSIVATION APPLICATIONS

The samples of pyrolytic Si_3N_4 of n-type GaAs described in AFWAL-TR-80-1149 received further analysis during this period. These samples were prepared in our cold-wall atmospheric-pressure reactor with rf-heated susceptor. Gas flow rates employed were as follows:

- SiH_4: 11 sccm
- NH_3: 3.6 slm
- N_2 carrier: 29 slm .

At the deposition temperature of 615°C, the deposition rate of the film was about 20 nm/min. Prior to deposition, the gas flows were stabilized with the substrate held at 315°C. The sample temperature was then ramped to the deposition temperature in ~9 sec. This procedure minimizes thermal decomposition of the sample prior to the beginning of film deposition.

A. EVIDENCE FOR INVERSION OF THE n-TYPE GaAs SURFACE UNDER PYROLYTIC Si_3N_4

We measured the C-V and G-V characteristics of these samples under illumination. The results suggest it might be possible to achieve a p-type inversion layer if a sufficiently high minority carrier generation rate is provided.

C-V behavior was measured from 100 Hz to 10 MHz for a device illuminated with light from a tungsten lamp filtered with a red Wratten No. 25 filter. The C-V data are shown in Figure 1(a). The data from 10 kHz to 10 MHz were obtained with the digital, automated system described in the previous report; the 100 Hz and 1 kHz measurements were made using the voltage source and voltmeter of the digital system, together with the capacitive measurement apparatus from our analog C-V system. G-V data from 10 kHz to 10 MHz are shown in Figure 1(b). Conductance data for 100 Hz and 1 kHz were not recorded.

The rise in the low-frequency capacitance for negative bias is the most notable feature of Figure 1(a). The dark C-V and G-V data for this device are shown for comparison in Figure 2. We interpret the rise in capacitance as evidence for formation of a p-type inversion layer. Response of the inversion layer charge to the ac voltage is apparently enhanced by lateral diffusion of photogenerated holes from the region around the capacitor electrode. Since the electrode is 250-nm-thick Al and is thus opaque, photogeneration directly under the electrode is precluded.

The low frequency capacitance under illumination decreased again for bias less than -20 V. A possible mechanism for this behavior is a depletion of inversion charge by conduction through the dielectric in competition with the indiffusion of photogenerated holes. Evidence supporting this hypothesis is provided by the illuminated and dark dc current density versus voltage (J-V) data shown in Figure 3. Substantial photocurrent is observed only for negative metal bias that corresponds to inversion. Furthermore, the illuminated J(V) curves of Figure 3(b) exhibit saturation beyond 20 V with a saturation current density that increases with light intensity. Since the steady-state concentration of holes, and hence the lateral hole diffusion current, increases with light intensity, the photocurrent saturation behavior is consistent with the hypothesis.

Removal of inversion charge by dielectric leakage also explains stable deep depletion behavior under inversion bias, as can be seen in Figure 2(a), and has been observed for other samples. The ideal high-frequency inversion capacitance is independent of bias for a sufficiently low bias sweep rate. Just such behavior is seen in the 100 kHz, 1 MHz, and 10 MHz data of Figure 1(a), where the capacitance saturates at ∿20 pF. However, for the dark C-V data of Figure 2(a), the capactiance first saturates at roughly 20 pF for increasing inversion bias and then, beyond ∿-12 V, decreases further. Note that

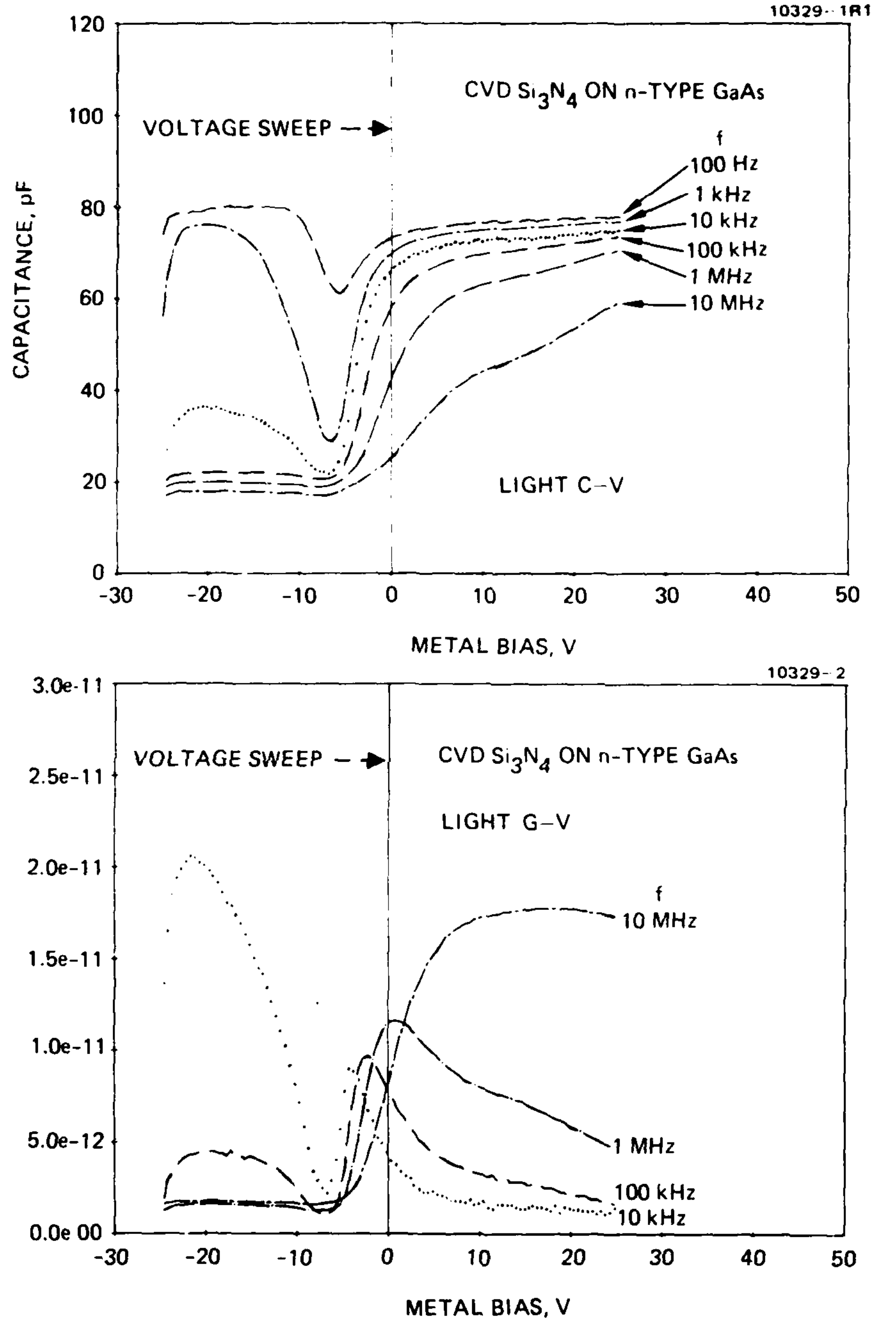

Figure 1. Electrical Behavior of Al/CVD Si_3N_4/n-GaAs MIS Capacitors under Illumination. (a) Capacitance-Voltage Characteristics. (b) Conductance-Voltage Characteristics.

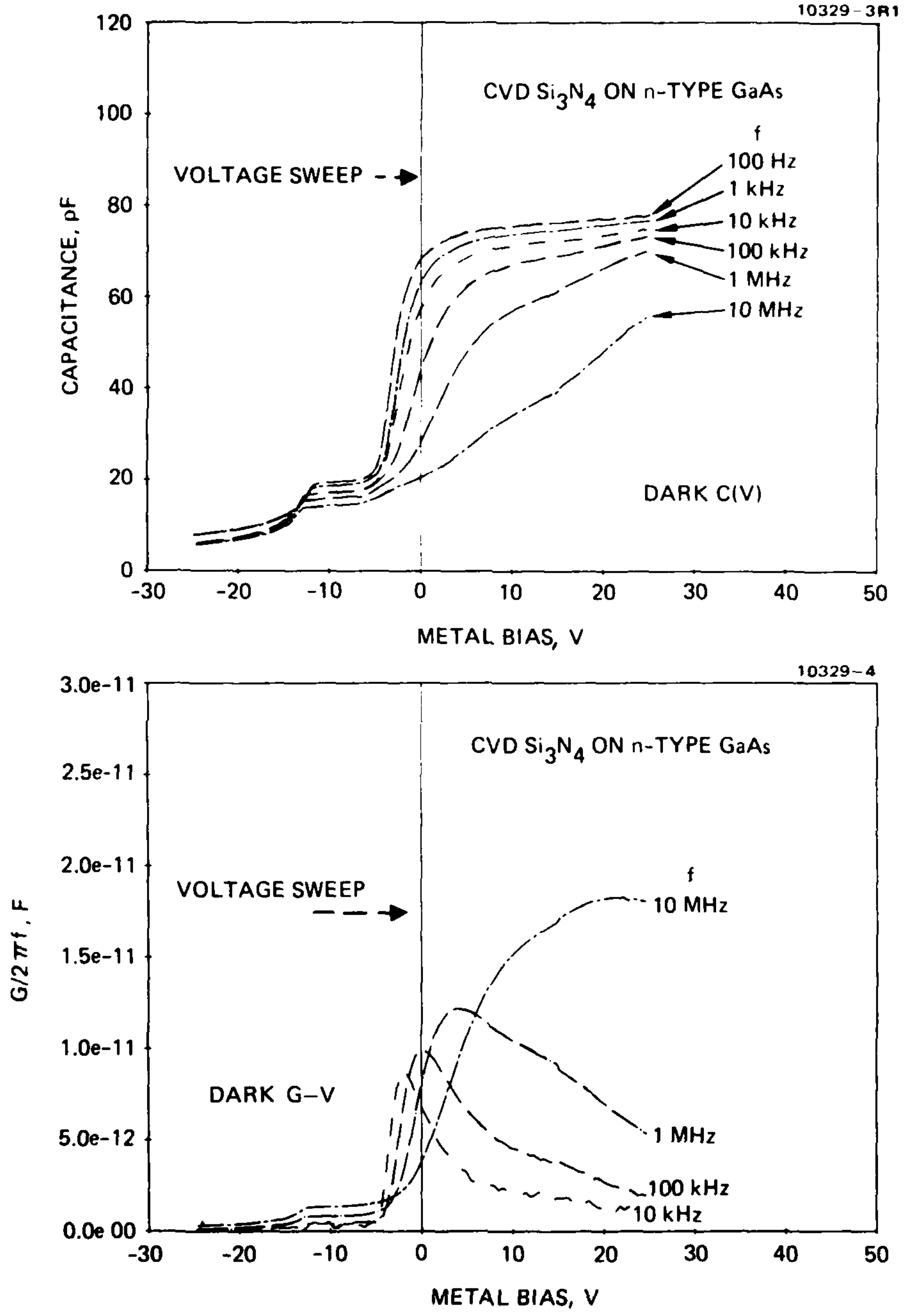

Figure 2. Electrical Behavior of Al/CVD Si_3N_4/n-GaAs MIS Capacitors in the Dark. (a) Capacitance-Voltage Characteristics. (b) Conductance-Voltage Characteristics.

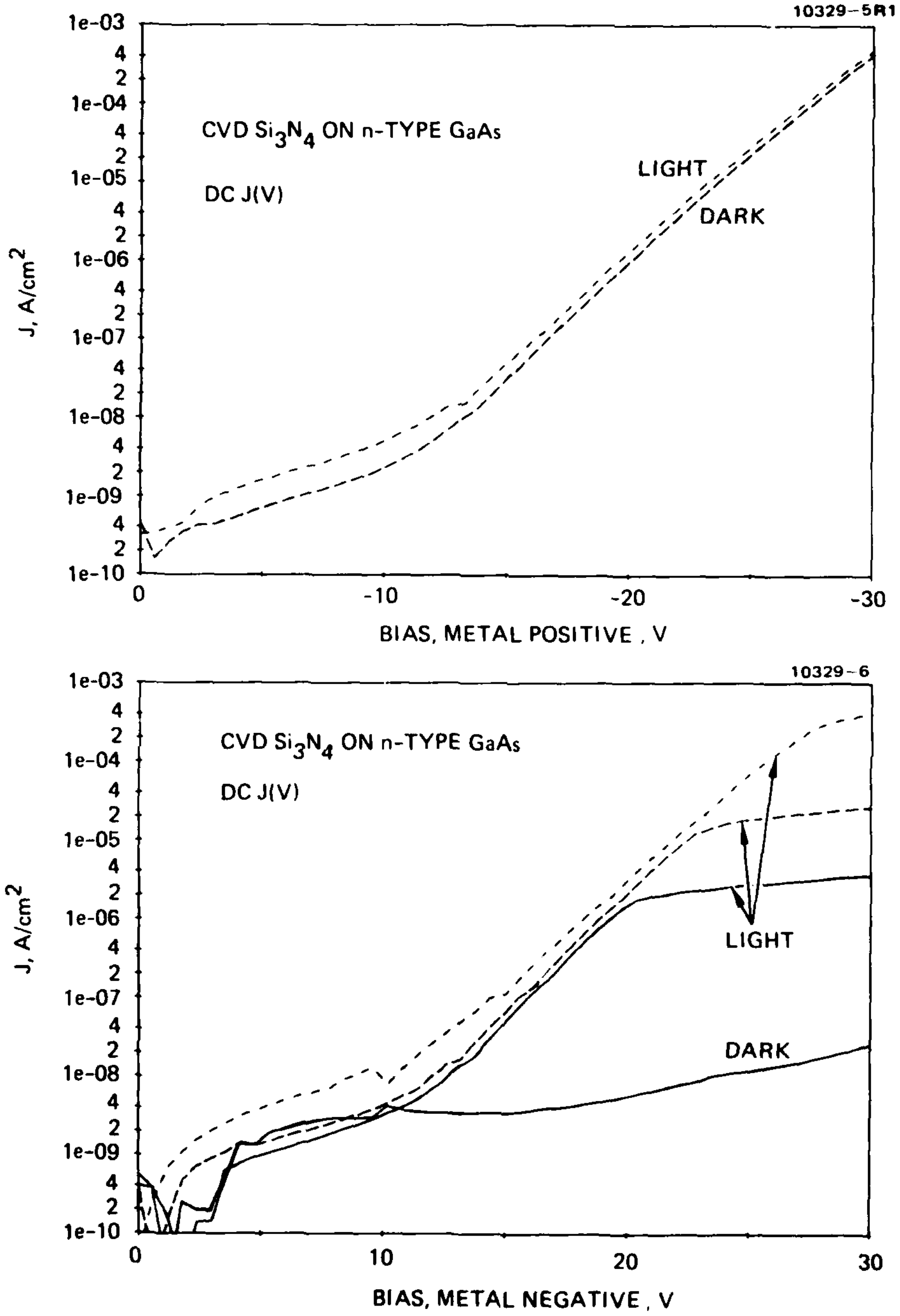

Figure 3. Current Density Versus Voltage Behavior of Al/CVD Si_3N_4/n-GaAs MIS Capacitors. (a) Accumulation Regime. (b) Depletion Regime.

-12 V corresponds approximately to the voltage at which the light and dark J-V curves of Figure 3(b) substantially diverge. Thus, deep depletion occurs when dielectric leakage of minority carriers surpasses the rate of thermal generation. The additional supply of minority carriers by photogeneration allows ideal high-frequency inversion behavior to be maintained to a greater bias voltage.

These results demonstrate that dielectric leakage must be considered when interpreting GaAs MIS C-V data. Compared to Si MOS with thermal SiO_2, we may expect higher leakage currents with deposited dielectrics and lower generation rates because of the greater bandgap energy of GaAs.

B. HYDROGEN PLASMA ANNEALING OF PYROLYTIC Si_3N_4

During this reporting period, we also investigated the effect of a hydrogen plasma anneal on the passivating behavior of pyrolytic Si_3N_4. This approach was suggested by published reports on improvement of the electrical and optical properties of poly-Si produced by H plasma annealing. The effect on poly-Si is thought to be due to hydrogeneration reducing the number of deep localized states.

The plasma anneal was performed in our modified LFE PND-301 reactor under the following conditions:

Temperature	300°C
Feed gas	H_2
Chamber pressure	1 Torr
RF power	250 W
Anneal time	30 min.

After annealing, MIS capacitors were formed by applying 0.29-mm-diameter Al electrodes and backside Ohmic contacts.

The measured C-V and G-V data are shown in Figures 4 and 5, respectively. Comparing these data with data for unannealed samples, no improvement due to the H plasma anneal is readily evident. Consequently, we have terminated studies of this procedure.

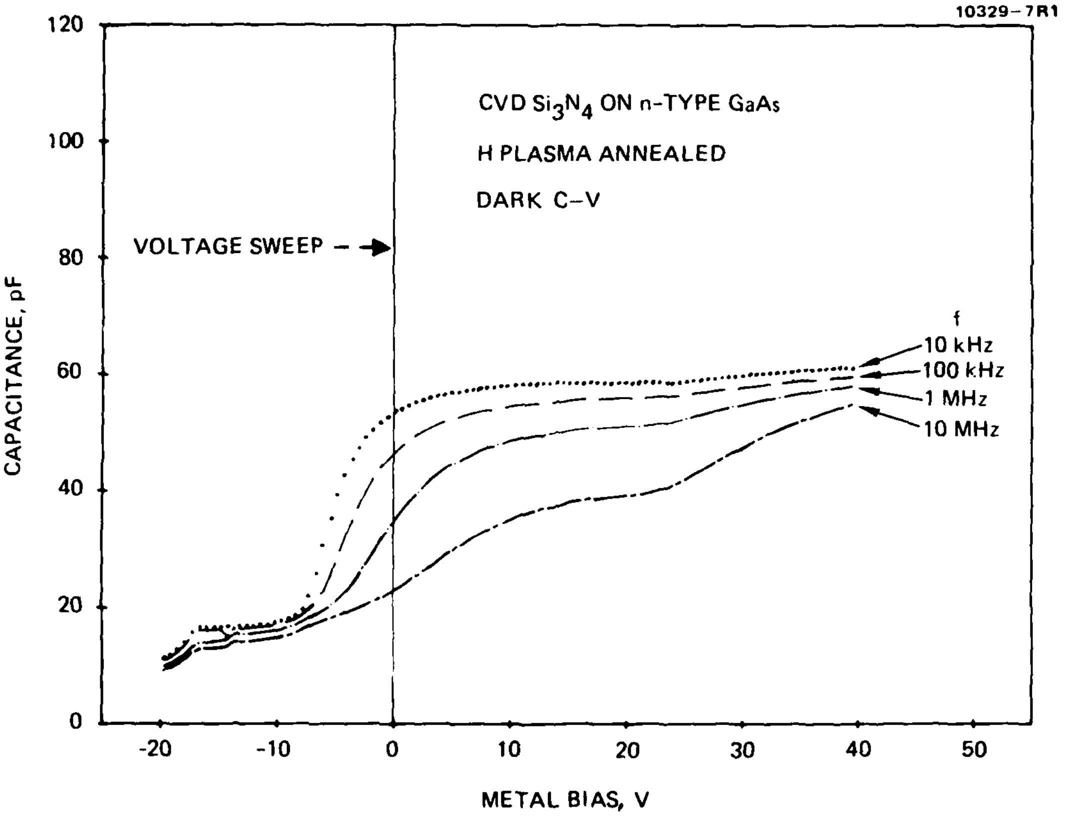

Figure 4. C-V Behavior of Al/H-Annealed CVD Si_3N_4/n-GaAs MIS Capacitors.

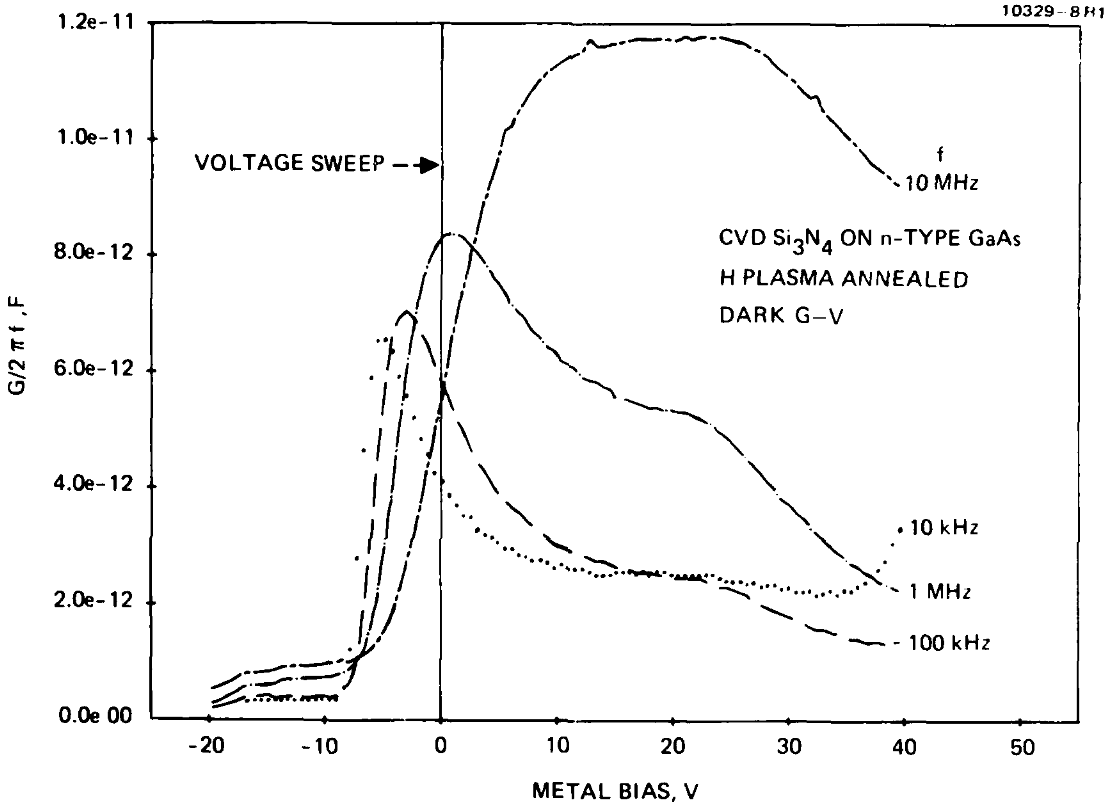

Figure 5. G-V Behavior of Al/H-Annealed CVD Si_3N_4/n-GaAs MIS Capacitors.

SECTION 3

PLASMA-ENHANCED-DEPOSITION PROCESS FOR SILICON NITRIDE

Successful operation of the large-scale high-vacuum-compatible plasma-enhanced-deposition (PED) system described in AFAL-TR-79-1234 has been demonstrated. A photograph of the system in the configuration first tested is shown in Figure 6. For reasons discussed below, a screen enclosure was constructed later to surround the reaction chamber.

With the system in the configuration shown in Figure 6, several trial runs were performed to locate the approximate operating range for depositing stoichiometric silicon nitride films. In our modified LFE reactor, approximate stoichiometry is achieved at 35 sccm of 1.5% SiH_4 in Ar, 4 sccm of N_2, 65 W rf power, and a total pressure of about 460 mTorr. Our new system has considerably greater pumping speed, permitting higher flow rates. Higher flow rates should assist in reducing oxygen contamination.

In our initial runs, we decided to hold the N_2 flow rate constant at 16 sccm and to study the effects of rf power and silane flow rate. The total pressure was held approximately constant at 250 to 300 mTorr by throttling the rotary pump. Lower pressures are desirable because they should result in more uniform deposition. All runs were performed with the hot plate temperature at 200°C.

The following deposition procedure was adopted. The system was evacuated to the 10^{-5} Torr range. Nitrogen was then admitted at 16 sccm and the system outgassed with a 50-W rf discharge for 10 min with the shutter closed over the sample. The pressure during this operation was maintained at 250 mTorr. The rf discharge was then shut off, diluted SiH_4 admitted, and the pressure adjusted by adjusting the throttle valve. The shutter was then opened and the rf discharge switched on. Depositions were performed for 20 min. The rf power, the SiH_4, and the N_2 were then shut off, in that order.

The following table summarizes the results obtained at 50 W rf power.

Flow Rate 1.5% SiH_4 in Ar, sccm	Film Thickness (Ellipsometric), nm	Deposition Rate, nm/min	Refractive Index
70	18	0.9	2.5
100	43	2.2	2.7
140	51	2.6	2.9

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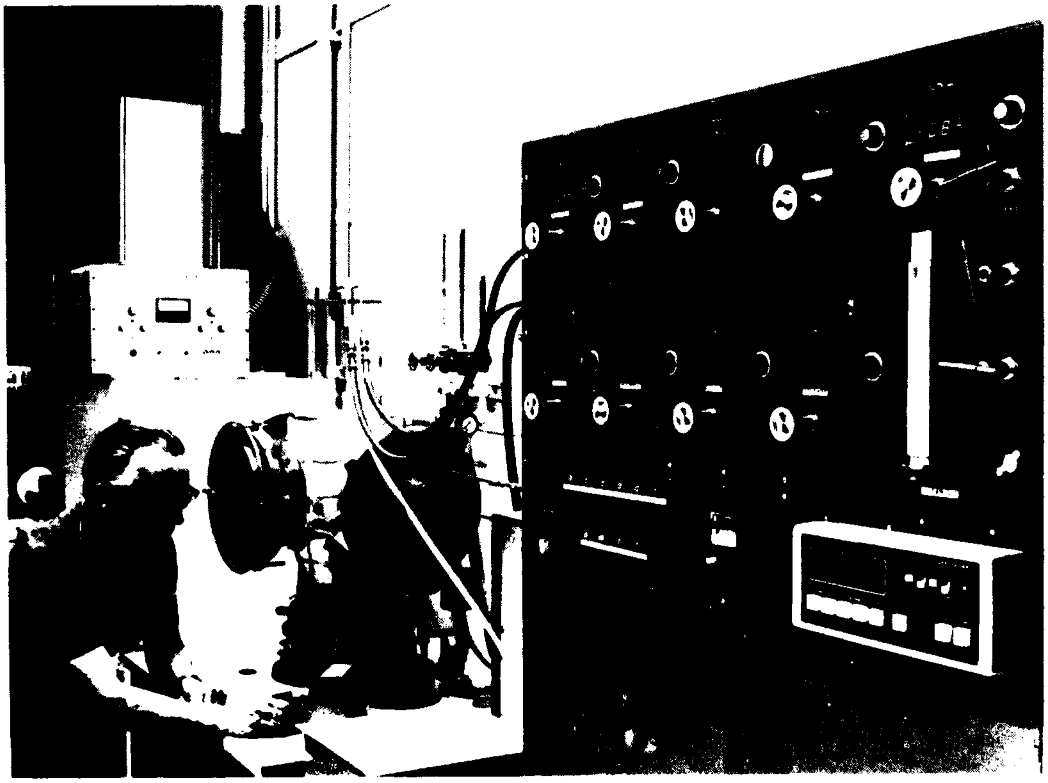

Figure 6. Large-Scale High-Vacuum-Compatible Plasma-Enhanced-Deposition System.

Since all these films were apparently Si rich and deposited very slowly, we concluded that the rf power was insufficient to excite the PED process properly. Accordingly, a run was performed at 100 W rf power and 100 sccm dilute SiH_4. This yielded a film with a thickness of 165 nm and a refractive index of 1.854. This index is slightly below that of stoichiometric Si_3N_4 (1.90 to 2.05). It therefore appears that the rf power level is a highly significant parameter.

Observations of system behavior indicated that the rf discharge was susceptible to modification in intensity and geometry by the configuration of grounding straps attached to the metal parts of the chamber. We therefore decided to stabilize the rf environment by erecting a screen enclosure for the system and providing simple, single, direct grounds for each metal fixture. The results obtained with these modifications were very satisfactory. The discharge became very stable, and disturbances to the system control electronics by the rf discharge were reduced to a negligible level.

A series of silicon nitride depositions to investigate the performance of the system in the new configuration was then initiated. Fifteen runs in this series were performed. Films were deposited on Si substrates and evaluated by ellipsometry to determine the deposition rate and to judge film composition. For this series, a standard procedure was adopted, and the parameters of the N_2 plasma preburn were fixed. All depositions were done at a hot plate temperature of 200°C and a system pressure of 0.25 Torr. The only parameters varied were the flow rates of SiH_4 + Ar and N_2, and the rf power.

Results of these runs were very satisfactory. Deposition rates for comparable gas flow and rf power conditions were substantially higher after the rf shielding and grounding modifications. For example, at 50 W rf, 100 sccm SiH_4 + Ar, and 16 sccm N_2, we obtained a deposition rate of 10.8 nm/min and an index of refraction of 1.74, whereas a rate of 2.2 nm/min and index of 2.7 were observed prior to the rf improvements for the same deposition parameters. It thus appears that the rf excitation efficiency was improved. Ellipsometric film properties nearest to Si_3N_4 were obtained at 30 W rf, 85 sccm

SiH_4 + Ar, and 16 sccm N_2. These parameters gave an index of 1.92 and a deposition rate of 7.1 nm/min.

After performing several more deposition runs and establishing deposition rates and refractive indices for growth conditions near those just listed, we determined a set of plasma silicon nitride deposition parameters that will serve as a base line for a parametric study. These parameters for the N_2 plasma preburn and the deposition are as follows:

- Nitrogen plasma preburn

N_2 flow rate	16 sccm
Chamber pressure	100 mTorr (13 Pa)
RF power	100 W
Hot plate temperature	200°C
Duration	10 min

- Deposition

N_2 flow rate	16 sccm
Flow rate of 1.5% SiH_4 in Ar	90 sccm
Chamber pressure	250 mTorr (33 Pa)
RF power	30 W
Hot plate temperature	200°C .

These parameters result in a deposition rate of about 7.5 nm/min and consistently give films with refractive indices between 1.90 and 2.05 at a wavelength of 632.8 nm.

Using the above parameters, films were deposited on pyrolytic carbon and examined by Rutherford backscattering (RBS). The RBS data indicated a Si/N ratio appropriate for Si_3N_4 and an upper limit on the O/N ratio of about 0.08.

During the next semester, our primary activity will be to study the effect of changes in sample preparation and growth conditions on the interface properties of PED silicon nitride on GaAs.

SECTION 4

PASSIVATION PROPERTIES OF PHOTOCHEMICALLY DEPOSITED SiO_2 ON GaAs

During this reporting period, a set of samples with photochemically deposited (PCD) SiO_2 was prepared. The depositions were Hg photosensitized, and substrate temperatures of 100°C and 200°C were employed. Substrates were prepared according to a standardized procedure that involves a solvent and HCl cleaning sequence followed by growth of 100 nm of anodic oxide. The substrates were stored and transported with the oxide in place. The oxide was removed shortly before dielectric deposition with 1 M NH_4OH followed by a de-ionized water rinse. Deposition and film parameters are given below.

	Run No. 517	Run No. 522
SiH_4 flow rate, sccm	2.0	2.0
N_2O flow rate, sccm	90	50
Substrate temperature, °C	200	100
Duration, min	12	10
Ellipsometric thickness, nm	205	136
Index of refraction (632.8 nm)	1.48	1.47

The ellipsometric parameters listed above are from measurements on the n-type GaAs samples, for which a substrate index of refraction 3.89-0.19i was used.

Capacitance and conductance data for these samples are shown in Figures 7 and 8. The behavior is generally typical of our results with deposited dielectrics (i.e., large frequency dispersion for accumulation bias and evidence of stable deep depletion). Illumination eliminated the deep depletion.

To concentrate the program effort on PED silicon nitride, it was agreed at a program review held at Wright Patterson Air Force Base on 19 March 1980 that further work on photochemically deposited dielectrics on this program would be terminated.

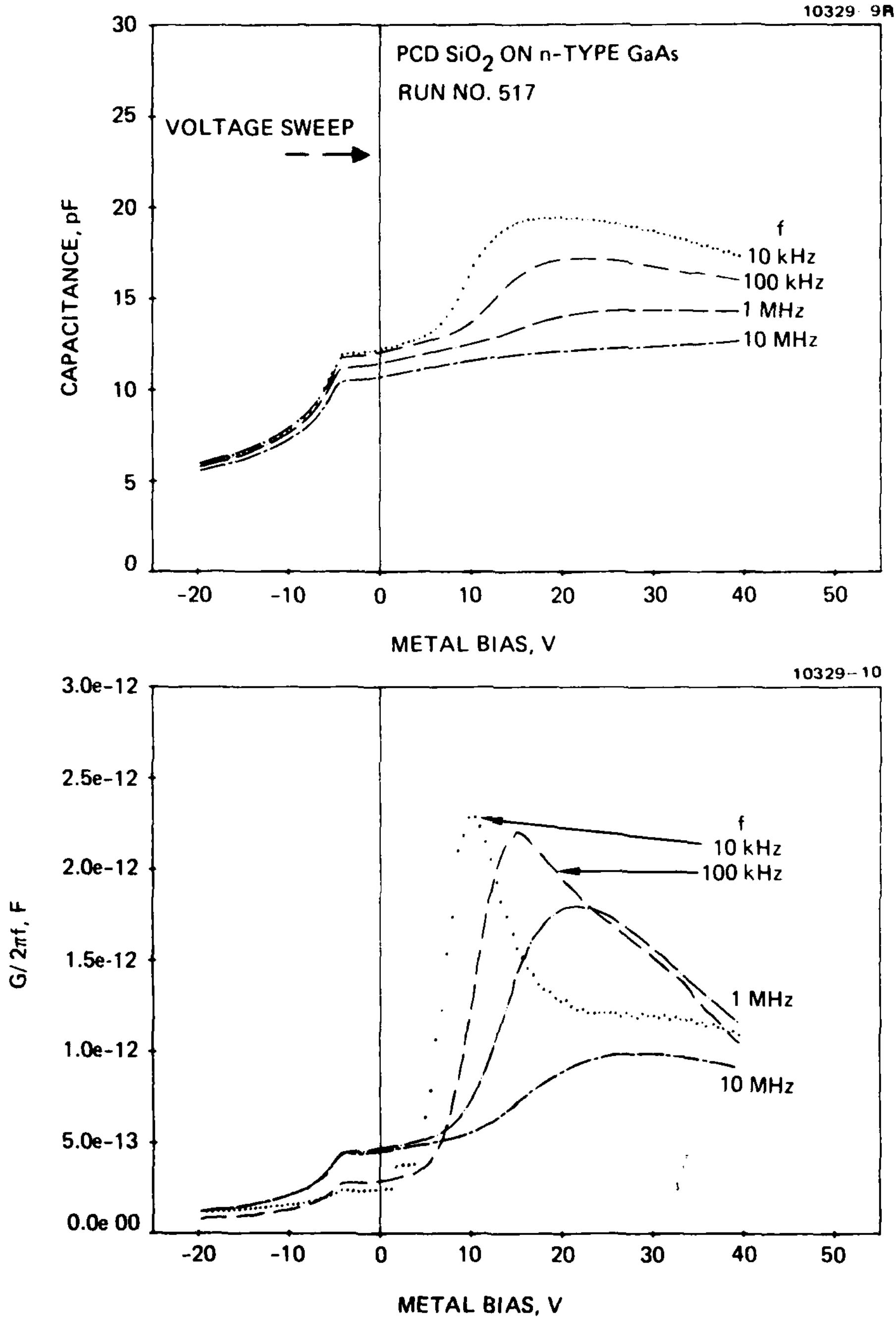

Figure 7. Electrical Behavior of Al/PCD SiO_2/n-GaAs MIS Capacitors. (a) Capacitance-Voltage Behavior. (b) Conductance-Voltage Behavior.

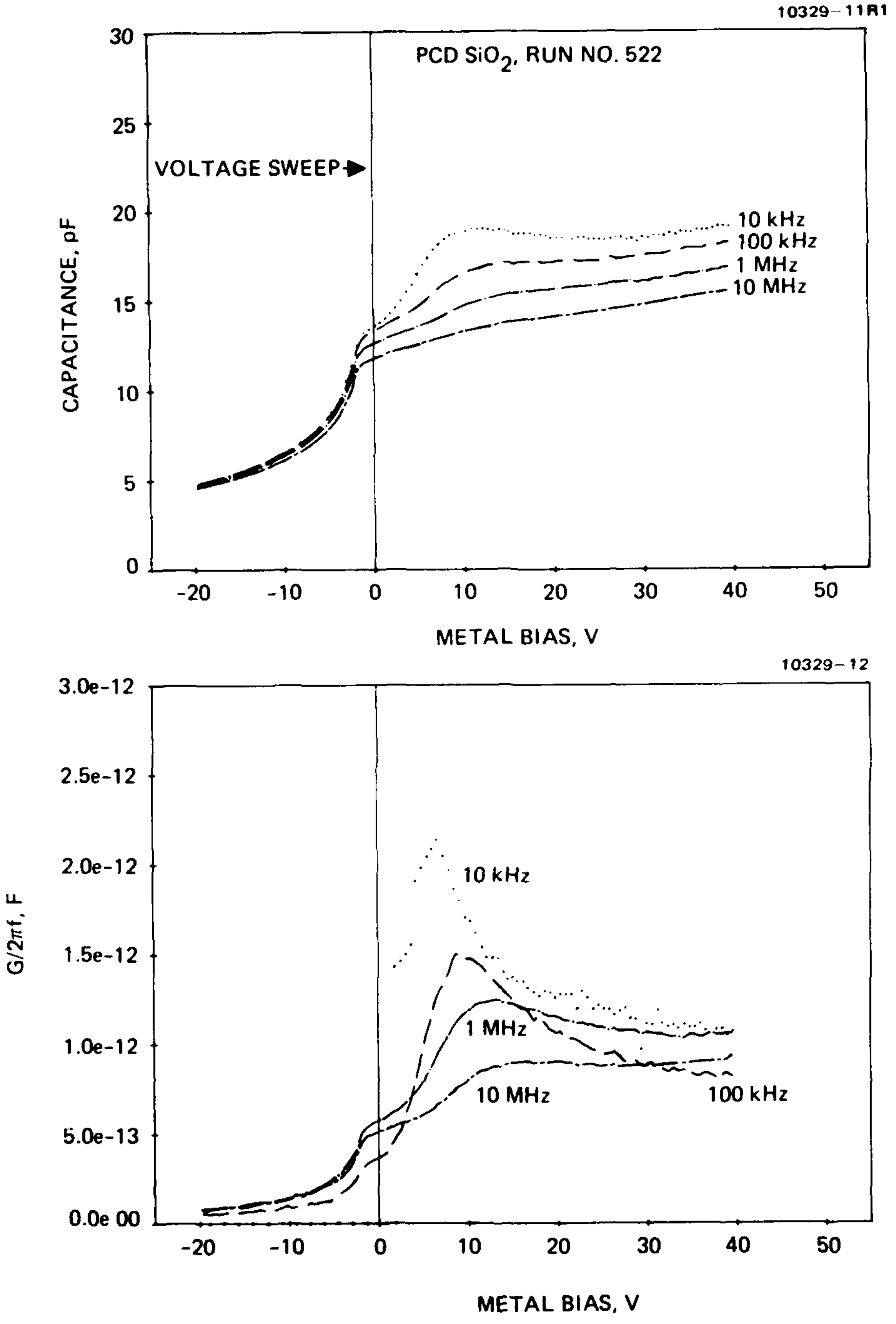

Figure 8. Electrical Behavior of Al/PCD SiO_2/n-GaAs MIS Capacitors. (a) Capacitance-Voltage Behavior. (b) Conductance-Voltage Behavior.

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