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**AN ELECTRON CYCLOTRON RESONANCE PLASMA PROCESS FOR InP
PASSIVATION**

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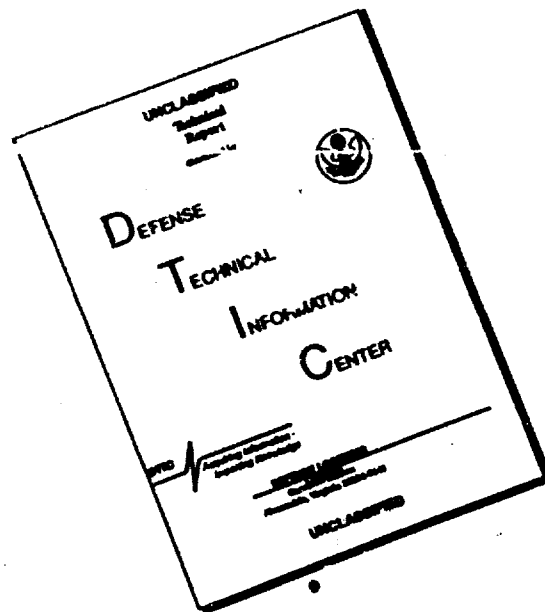
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ABSTRACT

In-situ ellipsometry has been used to monitor electron cyclotron resonance (ECR) plasma oxidation of InP at room temperature in the shadow plasma between a shutter and the sample. This process leaves no detectable excess P at the InP-oxide interface. A capping layer of SiO₂ was grown by ECR chemical-vapor deposition at a substrate temperature of 150°C. The samples were rapid-thermal annealed at 500°C for 1 min in an oxygen ambient. The dielectric layers were evaluated by current-voltage and capacitance-voltage measurements on metal-oxide n-type InP capacitors.

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Because of the microwave and optoelectronic applications of InP and related ternary and quaternary solid solutions, there are many possible applications for metal-insulator semiconductor field-effect transistors (MISFETs) using these III-V compound semiconductors. Many different processes for preparation of dielectric layers to provide more stable device properties have been reported since the early work of Lile and Collins¹ in 1976. Recently, Robach et al.² demonstrated that a 15 nm thick $\text{In}(\text{PO}_3)_3$ -like condensed phosphate grown by anodic oxidation followed by a 100 nm thick evaporated Al_2O_3 layer gave reduced drain-current drift. Unfortunately, wet anodic oxidation is not compatible with present microelectronic circuit fabrication processing. Therefore, in this paper, a dry process is described to produce an oxide surface layer by electron-cyclotron resonance (ECR) oxidation of InP at room temperature followed by the deposition of about 70 nm of SiO_2 by ECR chemical-vapor deposition (CVD) with SiH_4 and O_2 at 150°C.

The electronic passivation of semiconductor surfaces involves the reduction of surface electronic states. Simply stated, these states arise from the termination of the bonding network at the surface to produce intrinsic surface states sometimes called dangling bonds, and from defects and impurities which give rise to extrinsic or impurity states. For the Si surface, passivation is accomplished through the formation of a dielectric film, typically SiO_2 , which ties up the dangling bonds with the formation of an electronically innocuous wide gap insulator of high stability, reliability and stable stoichiometry. Thus, both intrinsic and extrinsic surface states are reduced to far below (10^{-2}) the usual number of carriers desired (minimum about 10^{12}) in inversion layers. For III-V's and other compound semiconductors, attempts at formation of passivating dielectrics has often led to an increase

of surface state density. The primary reason is that through reaction at the interface the formed dielectric, grown by oxidation or deposited, alters the stoichiometry of the semiconductor surface, thereby producing impurity states. Thus, it is the reactivity and fragility of the surfaces of compound semiconductors that has frustrated attempts at electronic passivation.

For GaAs and InP excess As and P, respectively, have precluded passivation using simple processes such as oxidation and CVD which were proven successful for Si. The ECR, plasma process used in this study is based on previous concepts by others^{1,2,3,4} and directly on the most recent work in our group^{5,6}. For compound semiconductors the surface stoichiometry changes during virtually all reactions. However, for brief and mild oxidation of InP, the stoichiometry of the semiconductor is preserved, but as the surface reaction proceeds the stoichiometry changes. For thermal oxidation, the change is predictable based on diffusion rate differences for In^{+3} and P^{3-} which migrate from the substrate outward during oxidation^{4,5}. Thus the initial reactivity of the InP surface species in oxidant is high, but once the initial oxide is formed, the transport rates are different enough to alter stoichiometry in the oxide formed at the oxide-oxidant interface. This situation is decidedly different from the oxidation of Si and Ge where oxidant migrates to the semiconductor-oxide interface. Another important fact is that ECR plasma oxidation of Si, Ge and InP resembles thermal oxidation at low process temperatures rather than electrochemical oxidation^{7,8}. Thus it is possible that ECR oxidation done at low process temperatures to reduce diffusion, and if not excessive, might produce a stoichiometric oxide to tie up intrinsic states without producing extrinsic states. The thin passivating layer can

then be capped without further interface reaction.

In this study, the growth of the small amount of passivating oxide before capping was investigated. This approach used an in-situ ellipsometer to monitor the interface during the initial stage of oxidation. In our ECR chamber in-situ observations of this process were made and the data analysis was performed using optical models^{7,8,9}. The veracity of the best fit models were checked using x-ray photoelectron spectroscopy, XPS, and promising samples were electrically checked using capacitance-voltage measurements at 1 MHz on metal oxide semiconductor, MOS, capacitors. The in-situ analysis capability was the key, and enabled a real time search for and adjustment of conditions to achieve the necessary "mildness" for passivation of InP.

The ECR plasma system and the automated rotating analyzer in-situ spectroscopic ellipsometer (SE) system⁹ were built in this laboratory. A special modification for this study was to add a shutter in between the plasma and sample as shown in Figure 1. Recently, a similar application appeared¹⁰ where a baffle was used to isolate the substrate from the direct plasma and thus reduce damage. Prior to the passivation procedure described below, the InP single crystal $\langle 100 \rangle$ oriented, n-type, lightly doped (10 ohm-cm for Fig. 4) substrates were chemically cleaned first with degreasing (trichloroethylene - 5 min, acetone - 5 min, methanol - 5 min) and then etching (HF (48%): methanol = 1:10 - 20 s, methanol - 2 min with ultrasonic agitation) to remove the native oxide. No heat treatments were done before or after insertion into the UHV process chamber.

The passivation process consists of two steps. The first step is a very mild ECR plasma oxidation in the shadow plasma between shutter and sample; this step is the key to

the process and if done correctly it leaves no detectable excess P at the InP-oxide interface. The second step is a mild ECR deposition of a protective or capping oxide, SiO₂, on the passivation oxide from step one above. The entire process is done in sequence without removing the sample.

For the initial oxidation the plasma conditions were 300W input RF power at 2.45 GHz, an oxygen pressure of 2×10^{-3} torr with a flow rate of 20 sccm. These conditions with the plasma to sample distance of 20 cm yielded an oxide thickness of 9 nm in 30 min and excess P at the InP-oxide interface as shown by the 130.9 eV peak in the XPS spectrum in Figure 2a. This result is typical of ECR oxidation of InP. To preclude this problem we used a 8 cm diameter shutter located 5 cm from the sample to block the direct plasma (see Figure 1). This arrangement isolates the plasma stream from the growth surface and minimizes direct impingement of energetic species upon the sample surface. The substrate current is 5 ma compared to 500 ma without the shutter and the sample temperature is 40°C as compared to 80°C without the shutter. Langmuir probe measurements with and without the shutter revealed similar electron temperatures (about 12 eV), and plasma potentials (about 20V) but the ion density is reduced by an order of magnitude (to about $2.9 \times 10^9 \text{ cm}^{-3}$) with the shutter closed. Also uv light from the plasma which is known to cause damage¹¹ is blocked. Even though the shutter is larger than the sample, the shadow plasma can cause oxidation but at a significantly slower rate, viz. producing 4 nm oxide in 30 min. Using this process no free P was seen by XPS as shown in Figure 2b. The 134 eV peak represents oxidized P, the 130 eV peak is for P in InP and the broad In peak is for In in the InP and oxidized. Figure 3 shows the two optical models that were used to

analyze the in-situ SE data for this oxidation procedure with the shutter between sample and plasma along with the usual ECR process without the shutter. We use a-InP to simulate P because we have no optical data for free P on the InP surface. Table 1 summarizes the result in terms of an unbiased estimator¹², δ , which measures the quality of the fit. It is seen that no interface layer is needed to obtain the best fit for the case using the shutter, in agreement with the XPS results.

With the formation of 3-4 nm of oxide from the ECR oxidation step, ECR CVD using SiH₄ with O₂ was used to deposit about 70 nm of SiO₂. For the CVD growth the microwave power was 400 W, substrate temperature of up to 150°C, O₂ and SiH₄ (3% in Ar) flow rates of 3 and 35 sccm, respectively and with a total process pressure of 3x10⁻³ Torr.

The final structure was 3 nm of ECR oxide with an overlayer of 70 nm SiO₂. Metallization was performed in a separate chamber using a Cr layer (for adhesion) followed by Au evaporation. Either no post metal anneal was done or rapid thermal anneal. High frequency (1 MHz) C vs V measurements were performed on a variety of samples.

Electrical measurements demonstrated that initial growth of the oxide required use of the shutter, and that rapid-thermal annealing at 500°C in O₂ for 1 min reduced the C-V hysteresis from 2.8 V to 0.80 V. The current-voltage measurements demonstrated that the SiO₂ was highly insulating with a moderate breakdown field of 1.5 MV/cm. The C-V behavior for the annealed sample at a measurement frequency of 1 MHz is shown in Fig. 4 together with the calculated curve for an ideal SiO₂ dielectric. The area of the Cr-Au electrode was 2.1 x 10⁻³ cm², and the substrate net donor concentration was $N_d^+ = 2.2 \times$

10^{14} cm^{-3} . The hysteresis would correspond to a fixed oxide charge of about $3 \times 10^{11} \text{ cm}^{-2}$. The difference in the ideal flat-band voltage and the measured flat-band voltage is within the uncertainty in the calculated flat-band voltage for the ideal oxide. Because the C-V curve goes to minimum capacitance and does not show deep depletion, the InP should be inverted at the SiO_2 -InP interface. The close agreement between the measured and calculated C-V curves suggests a low density of fast interface states.

In conclusion, it was found that use of a masking shutter permitted the growth of a thin layer of passivating oxide without detectable excess P at the SiO_2 -InP interface. The properties of the protective layer of ECR CVD SiO_2 were improved by RTA in O_2 . The in-situ ellipsometry greatly enhanced the ability to determine the conditions for growth of the initial oxide layer.

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Table I

Sample	Model	Top Layer	Bottom Layer	δ
Without Shutter	A	In ₂ O ₃ (5.46 nm)	In(PO ₃) ₃ 49% + a-InP 50% (3.88 nm)	0.0054
	B		In(PO ₃) ₃ 15% + In ₂ O ₃ 85% (8.46 nm)	0.0120
With Shutter	A	In ₂ O ₃ (2.01 nm)	In(PO ₃) ₃ 37% + a-InP 63% (1.54 nm)	0.0079
	B		In(PO ₃) ₃ 85% + In ₂ O ₃ 15% (3.32 nm)	0.0045

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Figure 1. Plasma System With Shutter

Figure 2. X-ray photoelectron spectra of electron cyclotron resonance plasma oxidized InP: (a) is direct plasma exposure and (b) is with a shutter between plasma and InP surface.

Figure 3. Best fit optical models used to obtain parameters from in-situ ellipsometric measurements. Model A is without the shutter and model B is with the shutter between plasma and sample.

Figure 4. Typical 1 MHz C-V traces for PECVD-SiO₂/ECR-Oxide/InP samples with and without a shutter in between plasma and InP surface. Dashed curve is calculated ideal C-V curve.

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Table I. Comparison of Fit of Optical Models.

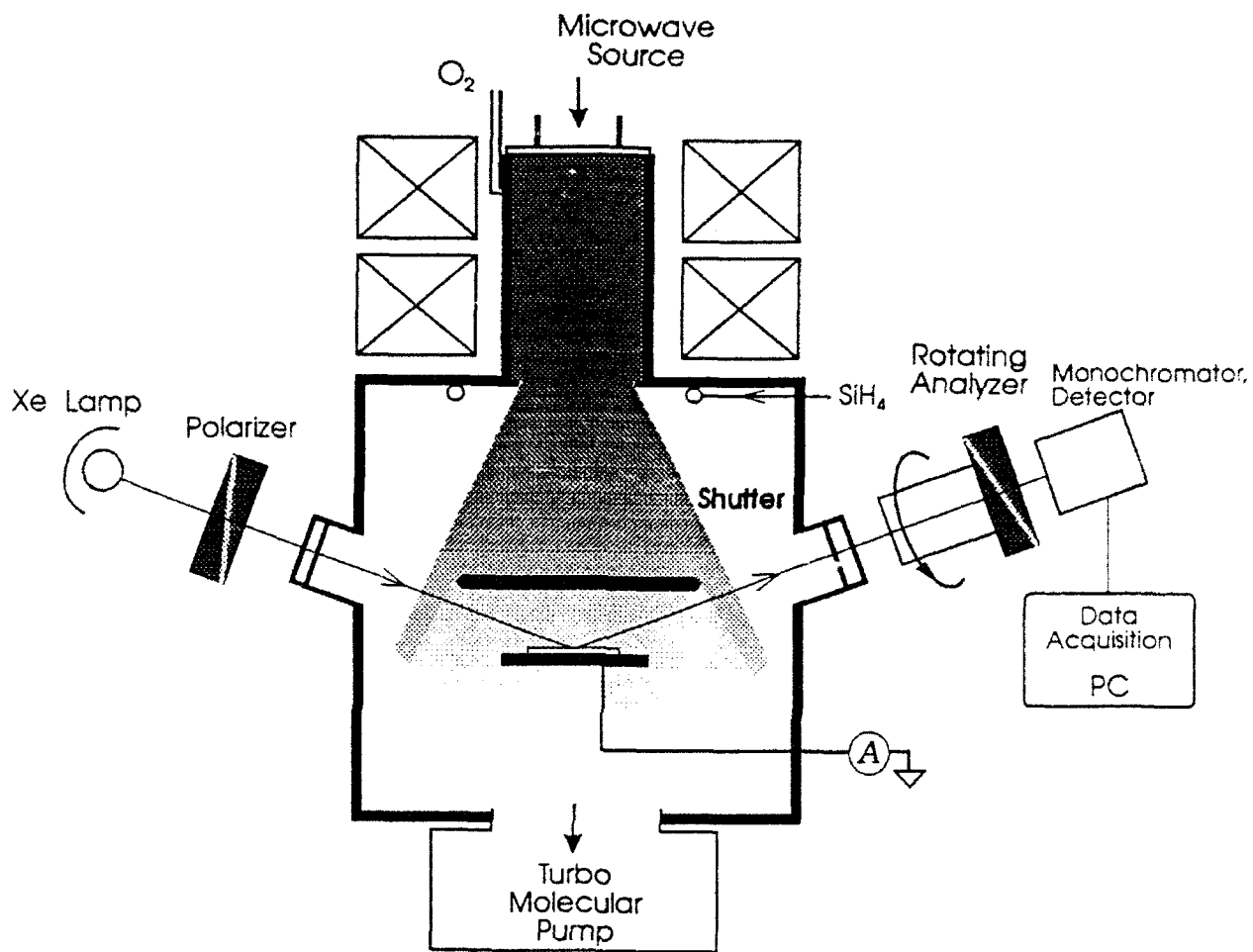
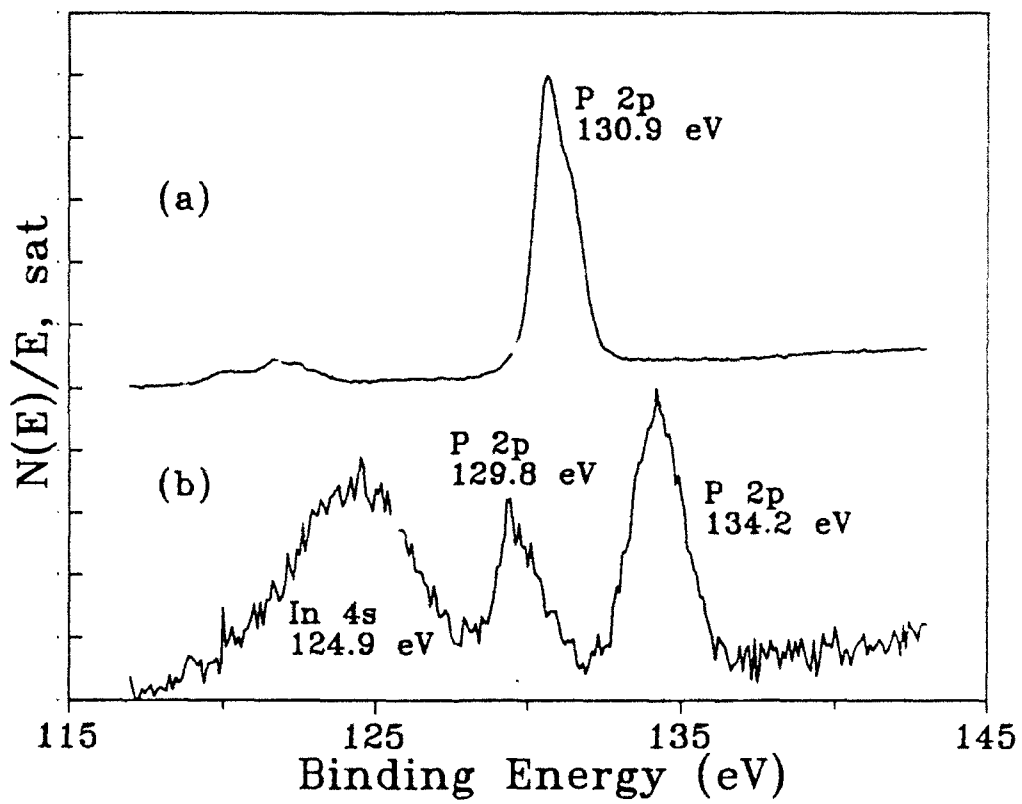
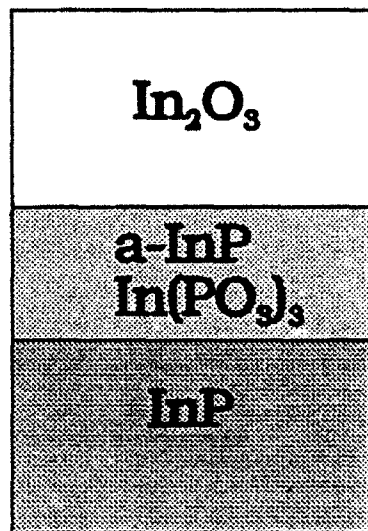
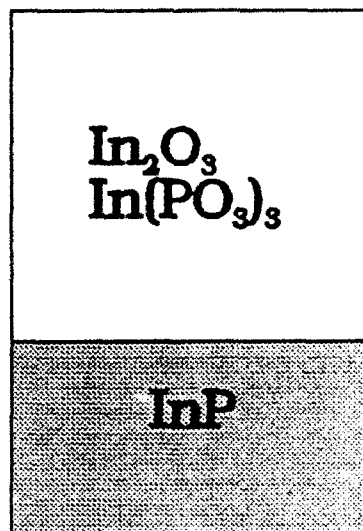


Figure 1

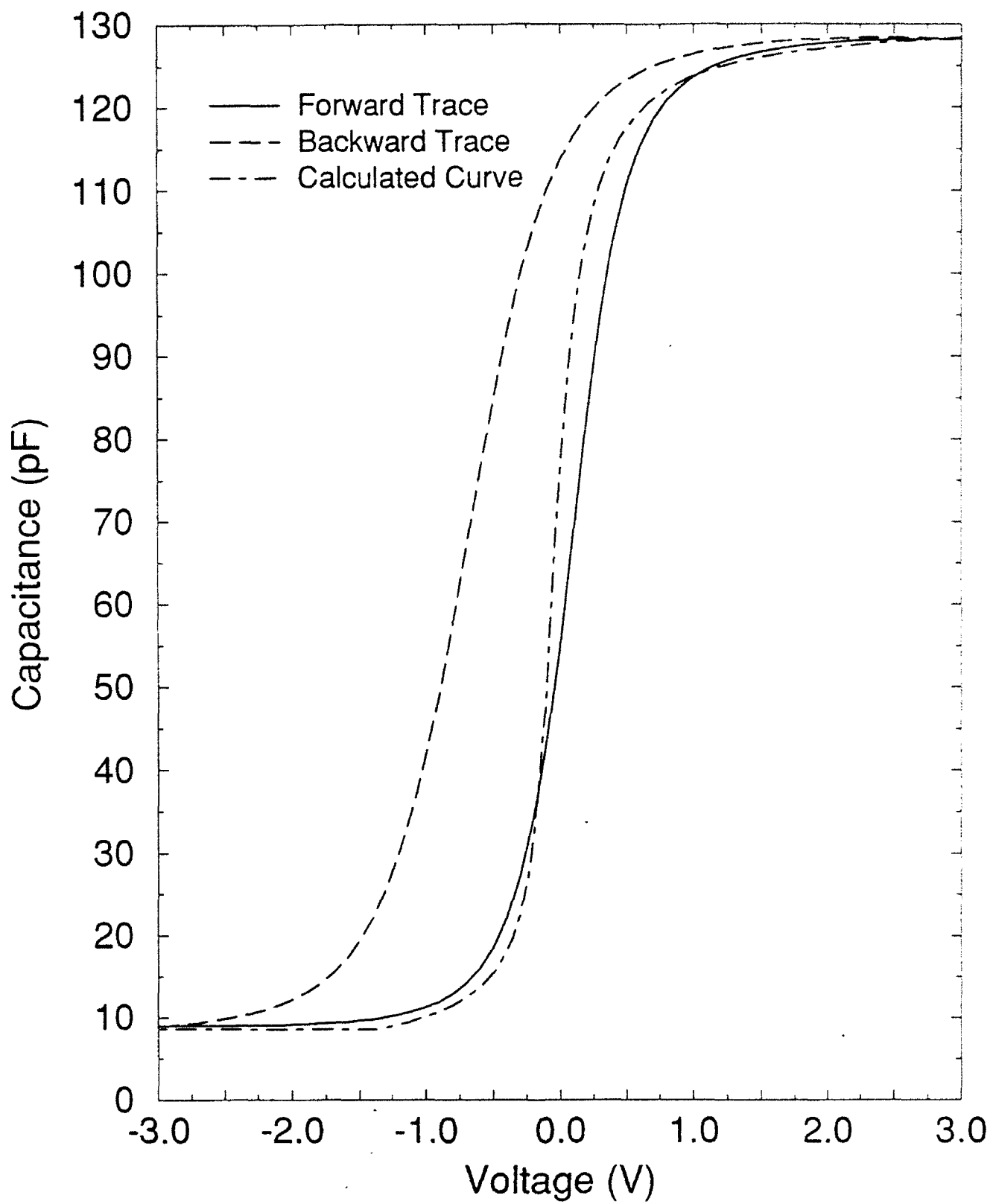




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1. D.L. Lile and D.A. Collins, Appl. Phys. Lett., 28, 554 (1976).
2. Y. Robach, M.P. Besland, J.J. Joseph, G. Hollinger, P. Viktorovitch, P. Ferret, M. Pitaval, P. Falcou and G. Post, Appl. Phys. Lett., 71, 2981 (1992).
3. L.G. Meiners and H.H. Wieder, Mat. Sci. Rep., 3, 139 (1988).
4. A. Nelson, K.Geib and C.W. Wilmsem, J. Appl. Phys., 54, 4134 (1983).
5. X. Liu, M.S. Denker and E.A. Irene, J. Electrochem. Soc., 139, 799, (1992).
6. Y.Z. Hu, J. Joseph and E.A. Irene, J. Vac. Sci. Technol. A, accepted for publication Jan. 1993.
7. Y.Z. Hu, J. Joseph and E.A. Irene, Appl. Phys. Lett., 59, 1353 (1991).
8. J. Joseph, Y.Z. Hu and E.A. Irene, J. Vac. Sci. Technol. B, 10, 611 (1992).
9. J.W. Andrews, Y.Z. Hu, and E.A. Irene SPIE Proc., 1188, 162 (1990). J.W. Andrews, PhD Thesis, Univ. of North Carolina, Chapel Hill, NC 1990.
10. T.T. Chau, S.R. Mejia and K.C. Kao, J. Vac. Sci. Technol. B, 10, 2170 (1992).
11. G. Hollinger, D. Gallet, M. Gendry, M.P. Bresland and J. Joseph, Appl. Phys. Lett., 59, 1617 (1991).
12. D.E. Aspnes, J.B. Theeten and F. Hottier, Phys. Rev. B, 20, 3992 (1979).