Plasma nitridation of thin Si layers for GaAs dielectrics

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(Received 13 November 1998; accepted 11 June 1999)

10–30 Å thick Si interface control layers (ICL) were deposited on GaAs epitaxial layers on GaAs substrates. These were then nitrided by exposure to an electron cyclotron resonance nitrogen plasma for varying times. The nitride thickness is shown to increase logarithmically with time. A model based on electron tunneling is proposed to explain the results. Capacitance–voltage measurements on resulting dielectric layers showed that, under optimal conditions, results adequate to fabrication of high-performance field-effect transistors are possible. The ICL thickness cannot be reduced to zero by nitridation because of damage to the underlying GaAs. © 1999 American Vacuum Society.

I. INTRODUCTION

Silicon nitride films have been widely used in silicon-based microelectronics devices as passivation layers, insulating barriers in thin film transistors, and diffusion barriers in multilayer devices. Recent work has focused on Si$_3$N$_4$ as a gate dielectric in GaAs-based metal–insulator–semiconductor (MIS) field-effect transistors (FETs). Initial work growing Si$_3$N$_4$ directly on GaAs by various techniques was unsuccessful due to damage to the GaAs surface. The unstable nitride/GaAs interface led to Ga and As outdiffusion and large numbers of midgap states at the GaAs/dielectric interface. Minimizing dangling bond states at the dielectric/GaAs interface is critical to unpinning the surface Fermi level from the GaAs midgap, and is required for successful FET operation. The problem was partially solved by growing an epitaxial Si buffer layer of optimal thickness on the GaAs by plasma-enhanced chemical vapor deposition (PECVD). Good results were obtained with low Si layer growth temperatures. This Si “interface control layer” (ICL) yielded MIS capacitors, with midgap trap densities as low as $10^{10}$ eV$^{-1}$ cm$^{-2}$. Unfortunately, the ICL did not produce good MISFETs, probably because the band offsets between Si and GaAs lead to a two-dimensional electron gas in the Si which prevents inversion in the GaAs.

In this work, we explore the possibility that the ICL can be thinned sufficiently by plasma nitridation to allow successful FETs without electron confinement in the ICL and with low midgap trap densities at the GaAs surface. Thus, the ICL becomes a sacrificial layer by which the interface state density can be controlled. To make this practical we determine the kinetics of Si nitridation and resulting interface state densities. Plasma nitridation was chosen because it has been shown to proceed at low temperatures forming high-quality Si$_3$N$_4$. An electron cyclotron resonance plasma source was used as it provides higher plasma densities, a higher fraction of the gas ionized, and low ion energies relative to conventional rf plasma sources. Interaction of N$_2$ with Si has been reported in a number of studies, one of which has shown that a very sharp and uniform amorphous Si$_3$N$_4$/crystal Si interface results.

II. EXPERIMENT

A Si ICL was deposited epitaxially on a 1 µm Be-doped GaAs epitaxial buffer layer ($p = 5.0 \times 10^{18}$ cm$^{-3}$) on a (100)-oriented Zn-doped GaAs wafer ($p = 1 \times 10^{18}$ cm$^{-3}$) as described previously. Before epitaxy the wafer was etched for ~40 s in HCl, rinsed under flowing deionized water for ~3 min, and bonded to a Mo substrate holder using In paste. The mounted wafer was loaded into the molecular beam epitaxy (MBE) facility. The vacuum system consists of six MBE chambers connected through an ultrahigh vacuum (UHV) transfer system to an x-ray photoelectron spectrometer and other instruments. All chambers have base pressures in the low $10^{-10}$ Torr range. Before ICL growth the wafer was heated to 873 K in an As$_2$ flux to thermally desorb the residual native oxide. X-ray photoelectron spectroscopy (XPS) verified that the buffer layer surface was clean before ICL growth.

Remote-plasma-enhanced chemical vapor deposition (RPECVD) was used both to deposit the Si ICL and subsequently to conduct nitridation and the final Si$_3$N$_4$ deposition. The system consisted of an electron cyclotron resonance (ECR) plasma source, coupled to a vacuum deposition chamber. The RPECVD system was pumped by ion and turbomolecular pumps and had a base pressure of $1 \times 10^{-10}$ Torr. He and N$_2$ were introduced at the top of the ECR chamber where the plasma was generated. SiH$_4$ was added to the gas phase through a “shower-head” located halfway between the aperture of the ECR chamber and the substrate. A low power (~60 W) SiH$_4$–He remote plasma, reportedly noncorrosive for the GaAs surface, was used to grow the silicon layer. The substrate temperature during growth was ~600 K and the pressure before the plasma initiation was 1.4 $\times 10^{-4}$ Torr. Partial pressures of 5.5 $\times 10^{-5}$ Torr SiH$_4$ and...
The substrate was radiatively heated from the back side and temperatures were measured with a thermocouple calibrated with an infrared pyrometer. The plasma was initiated by briefly closing the valve between the plasma chamber and the turbomolecular pump to increase the gas density. The valve was opened as soon as the plasma started. Pumping speed was controlled with the valve to adjust the gas pressure and deposition rate. After growth, the ICL was analyzed by XPS.

Nitridation of the Si layer was conducted in the same CVD chamber using N\textsubscript{2} and He gasses at a total pressure of 2\times10^{-4} Torr (5\times10^{-5} Torr He and 1.5\times10^{-4} Torr N\textsubscript{2}). The plasma power during nitridation was 350 W. The nitridation process was interrupted at various times and the sample was transferred to the XPS analysis chamber for characterization. Nitridation times as short as 1 s or as long as 15 min were used.

XPS data were compiled and analyzed in a Perkin–Elmer model 5400 XPS station that is connected to the MBE and the CVD chambers. The XPS is equipped with Mg and Al x-ray sources and uses a hemispherical energy analyzer. The x-ray power was 400 W and Al K\alpha radiation was used for all experiments unless otherwise noted. The dominant Al K\alpha x-ray emission occurs at 1486.6 eV with a linewidth of ~0.7 eV.\textsuperscript{8} The analysis area was ~10 mm\times1 mm. The binding energy (BE) scale and the Fermi level were calibrated against the Au 4f\textsubscript{7/2} (BE=84.00 eV) and Cu 2p\textsubscript{3/2} (BE=932.4 eV) core levels. Calibration spectra were acquired before and after each cycle of deposition and nitridation to assure consistency in the BE scale. The take-off angle (analyzer with respect to sample surface normal) could be varied from 20° to 70° for angle-resolved studies. Shadow peaks in the spectra resulting from the K\alpha\textsubscript{2} and K\beta x-ray emissions were removed by the data analysis software. The secondary electron background could also be removed in this way.\textsuperscript{9} Mixed Gaussian–Lorentzian curves were fit to the spectra including the fraction Gaussian character as a fitting parameter. A constant pass energy of 17.9 eV was used in the analyzer and the energy step was 0.1 eV in spectra. The resulting full width at half maximum (FWHM) of the Au 4f\textsubscript{7/2} was 1.15 eV, and the Cu 2p\textsubscript{3/2} was 1.55 eV. As(3d\textsubscript{5/2}), As(3d\textsubscript{3/2}), and Ga(2p\textsubscript{1/2}). Ga(2p\textsubscript{3/2}) peaks could be clearly resolved in all spectra. Fitting showed these peaks to have expected separations, widths, and intensity ratios.\textsuperscript{10,11}

After nitridation of Si ICLs, ~300 Å of Si\textsubscript{1}N\textsubscript{4} was deposited \textit{in situ} on the nitrided ECL using the same RPECVD system as was used for the Si deposition. All of the samples then underwent rapid thermal annealing (RTA) in dry N\textsubscript{2} at temperatures between 720 and 1370 K. Typical RTA conditions included heating rates of >35 K/s, anneal times of 15–60 s, and rapid radiational cooling (~15 s to <525 K). After removal from the MBE/CVD facility, aluminum top electrodes were evaporated onto the Si\textsubscript{1}N\textsubscript{4} and patterned photolithographically to form MIS capacitors, 300 μm in diameter. Finally, the samples were mounted on glass slides using indium, which also provided back contacts for electrical measurements. Capacitance–voltage measurements were carried out using an HP4284 LCR meter at the frequencies from 100 Hz to 1 MHz.

Following C–V measurements, cross-sectional transmission electron microscopy (XTEM) specimens were prepared. Samples were cleaved to provide two equal sized pieces and were glued together with the film sides facing each other. The glued pairs were cleaved into slabs approximately 1 mm thick and thinned by mechanical grinding and polishing down to tens of microns thickness. The samples were ion milled in a Gatan ion miller using two 5 kV, 7 mA Ar\textsuperscript{+} ion beams incident at 12° with respect to the sample surface. The samples were cooled to ~80 K during milling. The specimens were mounted on 3 mm copper rings and loaded into the TEM. A Philips CM-12 TEM was used to characterize the dielectric/GaAs interface.

### III. RESULTS

Angle-resolved XPS (ARXPS) measurements and reflection high-energy electron diffraction (RHEED) analyses of the GaAs surface prior to Si ICL deposition suggested an As-terminated surface as planned. This is generally the optimal surface for growth of a heteroepitaxial Si layer.\textsuperscript{12} Si was deposited by ECR CVD on the as-grown GaAs buffer layers. The crystallinity of the Si ICL was monitored during growth by RHEED and following growth by scanning tunneling microscopy (STM). The RHEED pattern of the as-deposited Si on GaAs with a Si thickness of 10–20 Å and a growth temperature of 625 K was a hybrid of (1×1) and (2×1) patterns. Heating of the film over 825 K resulted in partial hydrogen desorption and a (2×1) surface reconstruction.\textsuperscript{13} The STM

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**Fig. 1.** Montage of Si 2p XPS spectra obtained at a take-off angle of 50° for various nitridation times ranging from 1 to 880 s. Data for 1 and 2 s of nitridation have been smoothed.
images acquired after in situ annealing support our conclusion that the Si films are single-crystal layers that completely cover the GaAs surface.

The thickness of the Si was determined by XPS using the Si 2p, Ga 3d, and As 3d signals obtained at several angles. Ga and As 3d spectra were preferred because of the availability of a reference to known substrate signals. Si thicknesses were determined by fitting the change in the GaAs signal peak intensities with respect to take-off angle. In addition, the absolute intensity attenuation of specific GaAs peaks for each angle before and after Si deposition was used to determine the thickness. The latter proved more reliable because a large number of peaks with different take-off angles, kinetic energies, and hence escape depths could be compared. The final Si thickness was determined by averaging all values obtained. Angle-resolved measurements agreed in general with the results from GaAs signal attenuation but were significantly more noisy. Overall, thickness values for the initial ICL’s have an error of approximately ± 0.2 nm.

After characterization of the initial ICL layers, plasma nitridation was conducted in a series of short plasma exposures separated by XPS analyses. Figure 1 shows the XPS spectra of the Si 2p core level for a take-off angle of 50° after ECR plasma nitridation at 670 K for several lengths of time for the 30 Å Si ICL sample. Resulting peak positions and assignments are listed in Table I. No evidence was found for patchy or non-uniform nitridation.

The increasing intensity ratio of the Si (Si3N4) peak (101.9 eV) to the Si0 peak (99.0 eV) at large take-off angles showed the formation of Si3N4 on the Si ICL. This ratio was used to extract the thickness of the nitride layer. Assuming that a uniform layer of Si3N4 formed on the Si with an abrupt interface, the ratio of Si 2p intensities from the nitride and the Si layers, \( R(\theta) \), can be expressed as

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R(\theta) = \frac{I_{\text{Si3N4}}(E_{\text{Si 2p}}, \theta)}{I_{\text{Si}}(E_{\text{Si 2p}}, \theta)} = \frac{N_{\text{Si}}(\text{Si3N4}) \cdot \lambda_{\text{Si3N4}}(2p) \cdot [1 - \exp(-d_0/(\lambda_{\text{Si3N4}}(2p) \cos \theta))]}{N_{\text{Si}}(\text{Si0}) \cdot \lambda_{\text{Si}}(2p) \cdot [1 - \exp(-d_1/(\lambda_{\text{Si}}(2p) \cos \theta))] \cdot \exp(-d_0/(\lambda_{\text{Si}} \cos \theta))},
\]

where \( N_{\text{Si}}(\text{Si3N4})/N_{\text{Si}}(\text{Si0}) \) is the ratio of moles per unit volume of Si in the Si3N4 to Si in the Si, or \( 3V_{\text{mol}}(\text{Si})/V_{\text{mol}}(\text{Si3N4}) \), where \( V_{\text{mol}} \) is the corresponding molecular volume. \( \lambda_{\text{Si}}(2p), \sim 26 \AA,^{14} \) is the inelastic mean free path (IMFP) of Si 2p photoelectrons in Si and \( \lambda_{\text{Si3N4}}(2p) \) are \( \sim 30 \AA,^{15,16} \) for Si 2p photoelectrons in Si3N4 from Si–Si and Si–N bonds, respectively. \( d_0 \) and \( d_1 \) are the Si3N4 and Si thicknesses, respectively. Assuming no sputtering occurred during the nitridation, \( d_0 = (d - d_1) \cdot V_{\text{mol}}(\text{Si3N4})/3V_{\text{mol}}(\text{Si}) \), where \( d \) is the thickness of initially deposited Si layer. \( V_{\text{mol}}(\text{Si3N4}) \) and \( V_{\text{mol}}(\text{Si}) \) were obtained from density data of Si3N4 (3.44 g/cm3) and Si (2.33 g/cm3).\(^{17} \)

Figure 2 shows examples of fit curves and experimental intensity ratios after 10 s of nitridation. A complete set of fit results for nitride thicknesses versus nitridation time for a 30-Å-thick Si ICL is shown in Fig. 3. The accuracy of the resulting nitride thicknesses was estimated to be ± 0.5 Å (i.e., between the three curves shown in Fig. 2). The initial nitridation by the ECR plasma was rapid with formation of an \( \sim 14 \)-Å-thick layer of Si3N4 in 10 s. The subsequent nitridation rate decreased significantly, eventually becoming undetectable for experimentally achievable nitridation times. Similar behavior was found in low energy ion bombardment of Si,\(^{18} \) thermal nitridation with NH3,\(^{16} \) and pure N2 plasma nitridation of Si.\(^{19} \) From the results in
The pseudomorphic Si epitaxial layer directly in the TEM between Si and GaAs is too small to permit resolution of planes marked on the image. The difference in atomic numbers for the GaAs are clearly seen with one set of RTA at 725 K for 15 s prior to TEM analysis. The lattice thickness for a 4% lattice mismatch. Either the misfit dislocations never formed or they were removed after the nitridation when the epitaxial layer was again thinner than the critical thickness. One effect of the RTA may have been to allow these dislocations to move out of the film.

The nitridation rate as a function of time can be explained based on Mott’s theory of the formation of native oxide films on metals. In the Mott process, electron tunneling through the nitride is the rate-limiting step and Si$^{+4}$ is the predominant diffusing species, since it is much smaller than the negative ions of nitrogen. The tunneling probability $P$ is an exponential function of the nitride thickness,

$$\frac{dx}{dt} = P_0 \exp\left( -\frac{4\pi\sqrt{2mU}}{h} \right),$$

where $U$ is the energy barrier height and $m$ is the electron effective mass. Thus, the average tunneling time increases exponentially with thickness and consequently the thickness increases logarithmically with time. The tunneling probability is not an explicit function of temperature. However, at high temperatures more electrons cross the barrier thermionically rather than by tunneling, increasing the rate gradually. It is thus expected that higher substrate temperatures would accelerate growth. This is consistent with the typical behavior of logarithmic reaction processes observed here.

As plasma nitridation proceeded, the nitride contribution to the Si 2p XPS peak shifted gradually to higher energy. At the same time an oxygen 1s peak appeared and increased in magnitude. Plots of the N 1s and O 1s peak intensities (without correcting for x-ray emission cross section) are shown in Fig. 5. Apparently, as plasma treatment proceeded, nitridation was eventually superceded by oxidation as the dominant process.

The use of ultrahigh purity nitrogen, the low base pressure in the RPECVD chamber, and mass spectrometric analysis indicated that the initial process gas was not the source of oxygen contamination. However, as plasma treatment continued the nitrogen plasma apparently gradually etched the quartz window where the microwaves were introduced into the chamber. This resulted in accumulation of oxygen in the plasma. Because oxygen is more reactive with Si than is nitrogen, oxidation gradually replaced nitridation. The presence of oxygen contamination in the nitride and the limited energy resolution of our spectrometer explains the apparent Si 2p peak shift. The continuous shift in the Si-nitride peak...
rather than appearance of oxide peaks suggests that an oxynitride alloy resulted from the oxygen contamination. Similar oxygen contamination was also noticed in two recent studies. There the oxygen source was attributed to sputtering of the quartz windows through which microwave energy was introduced. Detailed examination of the Si 2p spectra for 10 s of nitridation revealed no detectable SiO 2 signature. As nitridation slowed and oxygen accumulated in the plasma, and oxygen increasingly replaced nitrogen in the dielectric layer. The lack of obvious change in reaction rate as oxygen content in the dielectric increases supports the tunneling model which is most strongly dependent upon dielectric thickness and not as dependent upon dielectric chemistry.

Prolonged plasma nitridation of the ICL not only caused oxygen contamination in the resulting dielectric but also damaged the dielectric/GaAs interface. Plasma treatment of a 20-Å-thick ICL for 1440 s resulted in complete reaction as verified by the absence of a Si 0 peak in the Si 2p spectrum. In addition, the As 3d spectrum was found to have changed, see Fig. 6. New 3d 3/2 and 3d 5/2 peaks appeared, consistent with formation of thin As oxides and nitrides. The contribution due to the As oxide increased with increasing angle with respect to the surface which suggests that the As oxide was near the sample surface. No changes in the Ga spectra were observed during plasma treatment for long times.

In a study of NH 3 plasma nitridation of the GaAs(100) surface, Masuda et al. reported the formation of an As–N layer and a Ga–As–N compound layer at low substrate temperatures (<373 K), while high substrate temperature (>473 K) formation of GaN and desorption of As were observed. In another report, Jones et al. found GaN formation exclusively at high substrate temperatures (~723 K). The low concentration of N in the Ga–As–N layer and exclusion of As were explained both by the miscibility gap of GaN–GaAs (Ref. 26) and the As vapor pressure. GaN was not observed in the current work. However, since the chemical shift (0.4 eV) of Ga 0 to GaAs could not be positively resolved in the study, it is still possible that Ga was present on the surface. To test the possibility that As and Ga could diffuse through the Si 3N x, a Si 3N x/Si/GaAs structure was annealed at 1020 K for 60 s. Both Ga and As were found to have diffused to the surface during this process. Ga 0 and GaO x were identified on the surface, while As desorbed.

C–V measurements were carried out on samples nitrided at various temperatures and annealed under different post-nitridation conditions. Optimal electrical properties were obtained on a sample nitrided at 300 K for ~1800 s and post-nitridation annealed at 900 K for 15 s. The C–V results for the optimal device are shown in Fig. 7. The hysteresis was <50 mV for both 1 MHz and 1 kHz C–V curves, and the
frequency dispersion was near zero. The “frequency dispersion” is defined here according to standard practice based on the voltage difference between $C-V$ curves measured at 1 MHz and 1 kHz at a capacitance equal to the flatband value $C_{\text{FB}}$. Annealing above 1000 K usually led to a much worse interface, while annealing below 900 K did not significantly alter the defect densities. Many devices had relatively large hysteresis values indicating negative charge trapped in deep states at the dielectric/semiconductor interfaces. Large frequency dispersions also were found suggesting strong Fermi level pinning away from the conduction band minimum.\textsuperscript{27}

The quasi-static $C-V$ curve for the best device (Fig. 7) shows normal accumulation, depletion and inversion. From the room-temperature conductance loss characteristic, $(G/\omega)$ versus angular frequency ($\omega$), the density of interface states $D_{\text{it}}$ was extracted using: \textsuperscript{27}

$$D_{\text{it}} = \left(\frac{G}{\omega}\right)_{\text{max}} \left[ f_p (\sigma_s) qA \right]^{-1},$$

where $f_p$ is a universal function, a function of the standard deviation of band bending ($\sigma_s$), and $A$ is the area of the capacitor. The value of $f_p$ used here was 0.46.\textsuperscript{28} A minimum conductance/angular frequency peak of 5.2 pF was obtained at a gate bias of -0.45 V corresponding to $D_{\text{it}} \approx 3 \times 10^{11} \text{eV}^{-1}\text{cm}^{-2}$ at the center of GaAs energy gap. For a practical Si CMOS circuit, the $D_{\text{it}}$ is $\sim 10^{11} \text{eV}^{-1}\text{cm}^{-2}$. Therefore, the defect density at this GaAs interface is sufficiently low for normal MISFET operations.

IV. CONCLUSIONS

We conclude that plasma nitridation of a Si ICL can be used to reduce the thickness of the ICL prior to PECVD deposition of a dielectric. The resulting nitride can have low enough interface-state densities under optimal processing conditions to provide adequate FET performance. Further optimization may additionally reduce the interface state densities. The nitride on the ICL provides protection for the ICL material during the PECVD process, which may be important in reducing damage to the ICL. It also protects the ICL from oxidation in case of air exposure. Excessive nitridation of the ICL can damage the GaAs substrate with consequent reductions in performance. Thus, it is unlikely that this method can be used to reduce the ICL thickness to zero. The appearance of oxide during nitridation suggests that it is advisable to coat the nitridation chamber with Si$_3$N$_4$ prior to use and to clean the process gas to the maximum extent possible, especially for long nitridations.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Department of Energy under Contract No. DEFG02-91ER45439. The microanalysis was carried out in the Center for Microanalysis of Materials at the University of Illinois, which is supported by the U.S. Department of Energy.