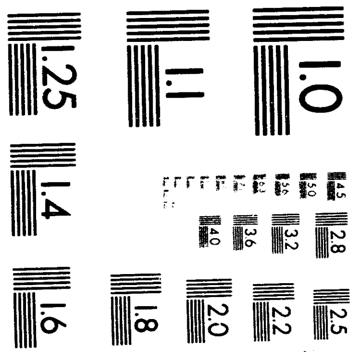
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ECR PLASMA SYNTHESIS OF SILICON NITRIDE FILMS ON GaAs AND InSb

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ABSTRACT

The growth of high-quality dielectric films from Electron Cyclotron Resonance (ECR) plasmas provides for low-temperature surface passivation of compound semiconductors. Silicon nitride (SiN_x) films were grown at temperatures from 30°C to 250°C on GaAs substrates. The stress in the films was measured as a function of bias applied during growth (varied from 0 to 200 V), and as a function of sample annealing treatments. Composition profiles of the samples were measured using ion beam analysis. The GaAs photoluminescence (PL) signal after SiN_x growth without an applied bias (ion energy ≅ 30 eV) was twice as large as the PL signal from the cleaned GaAs substrate. The PL signal from samples biased at -50 and -100 V indicated that damage degraded the passivation quality, while atomic force microscopy of these samples showed a three fold increase in rms surface roughness relative to unbiased samples. The sample grown with a bias of -200 V showed the largest reduction in film stress but also the smallest PL signal.

INTRODUCTION

The growth of high-quality dielectric films is important for the surface passivation of III-V compound semiconductors which can enhance the performance of microelectronic and optoelectronic devices made from these materials. For example, silicon nitride passivation of GaAs and InSb is useful for photovoltaic and infra-red devices, respectively. Chemical vapor deposition (CVD) yields high-quality dielectric Si_3N_4 films, but CVD employs temperatures which are incompatible with compound semiconductors. A low-temperature process is required for passivation of GaAs and InSb because the GaAs surface decomposes with vacuum annealing above 475°C and the InSb surface is unstable above 250°C [1]. In this study, an Electron Cyclotron Resonance (ECR) plasma was used to make SiN_xO_y passivation layers on GaAs and InSb because the ECR process offers low growth temperatures, and because the sample bias (i.e., ion energy) could be varied independently from other growth parameters. The desirable surface passivation properties include: resistance to chemical attack, low leakage current, high breakdown voltage, control of fixed charge and charge trapping, and low dielectric/semiconductor interface-state densities. Previously [2], MIS gate-quality dielectric Si_3N_4 films were deposited from a SiH_4/N_2 gas mixture at 200°C on Si substrates in our ECR plasma system. In this paper, we extend this work with Si to examine the ECR growth of SiN_x on GaAs and InSb.

The quality of a surface passivation layer is dependent upon both the effective elimination of surface states, and upon the mechanical and chemical robustness of the dielectric layer during device processing. High levels of stress in ECR-grown SiN_x can cause de-adhesion during device processing and therefore yield an ineffective passivation layer. In this study, GaAs and InSb are two model substrates which exhibit different SiN_x adhesion characteristics. Thermodynamic calculations indicate that the interface bonding between InSb and Si_3N_4 is weaker than the bonding between GaAs and Si_3N_4. Our previous work [3] has shown that the de-adhesion on InSb substrates can be alleviated by the addition of oxygen to the growth process, forming a

silicon oxynitride with stronger interface bonding. However, the SiN_xO_y layers have different material properties than SiN_x layers, and therefore other processes are required to lower the stress and improve the adhesion of SiN_x to compound semiconductors.

EerNisse [4] demonstrated that post-growth ion irradiation of CVD SiN_x on Si substrates changed the film stress from 1500 MPa (tensile stress, as-grown) to a saturation level of -3500 MPa (compressive stress). This large change from a tensile to compressive stress suggests that ion irradiation may be useful for controllably altering the state of stress in ECR SiN_x films grown on GaAs and InSb. Therefore, the effects on stress and passivation quality of energetic-ion treatments during the growth of SiN_x on GaAs were examined.

EXPERIMENTAL

The three (100)-oriented substrates used in this experiment were undoped semi-insulating GaAs, Si-doped ($1x10^{15}$ cm^{-3}) n-type (100) GaAs, and n-type InSb with a resistivity $\approx$ 0.05 Ω-cm. The GaAs was cleaned in acetone for 5 min., isopropyl alcohol for 5 min., deionized water for 15-30 sec., and then the surface oxide was stripped in a solution of 1 NH_4OH: 20 H_2O. The GaAs substrates were immediately loaded for ECR SiN_x growth at temperatures between 35°C and 250°C. The InSb was similarly cleaned in acetone, methanol, and deionized water. The surface oxide was stripped in a solution of 1 HF: 7 NH_4F and then the substrate was etched in a solution of 1 HNO_3: 5 lactic acid immediately prior to loading for ECR SiN_xO_y growth.

The plasma-growth system consisted of an ECR source attached to a reaction chamber with the substrates positioned 32 cm downstream from the ECR region in the source (defined as the position where the magnetic field equals 875 Gauss). The magnetic field was produced by two separate coils surrounding the ECR chamber, with one coil centered about the end of the ECR chamber (at the quartz vacuum window) and the other coil separated from the first by 8 cm. For these experiments, the magnetic field was maximum at the vacuum window and decreased along the axis with the ECR condition established at 8 cm from the quartz window. Microwave power (50-100 Watts) at a frequency of 2.45 GHz was transmitted to the ECR plasma chamber through the quartz window. The base pressure of this system is typically $5x10^{-9}$ Torr and the operating pressure was $2x10^{-4}$ Torr. A gas mixture of 15% SiH_4 in N_2 was introduced into the ECR chamber near the quartz window at a combined flow rate of 19 sccm. The two dominant ion species in the plasma were N_2^+ and H_2^+. For the growth of SiN_xO_y films, O_2 gas was introduced at a flow rate of 1 sccm from a gas ring also near the quartz window.

The samples were either electrically isolated relative to ground (the chamber walls) or biased negatively during growth in order to generate more energetic ions. In separate experiments [5], the ion energy incident upon the sample was determined to be $\approx$ 30 eV for the case of electrical isolation. The DC bias voltages used in these experiments were 50, 100, and 200 V; corresponding to ion energies of approximately 80 eV, 130 eV, and 230 eV. The sample temperature was monitored by a thermocouple bonded to a stainless steel foil adjacent to the sample, but electrically isolated from the sample. For T>50°C, the temperature was held constant during the deposition by radiatively heating the back of the sample. Composition analysis of each layer was obtained from 3.5 MeV He^+ Rutherford backscattering spectrometry (RBS) at a scattering angle of 164°, and 24 MeV Si^{+5} elastic recoil detection (ERD) at a scattering angle of 30°. Film stress (σ) was determined from the change in the radius of curvature of the substrate after growth, as given by [6]: $\sigma = [E/(1-\nu)]h^2/(6Rt)$, where E is Young's modulus of elasticity, ν is Poisson's ratio, h is the substrate thickness (331 to 533 μm thick), and t is the film thickness. The film thicknesses determined from polarization-resolved ellipsometry agreed well with thicknesses determined from RBS. The value of R is $R=(1/R_2-1/R_1)^{-1}$, where R_1 is the substrate radius of curvature before film growth and R_2 is the radius of curvature after the film growth. Note, the value for $E/(1-\nu) = 1.239 \times 10^5$ MPa for (100) GaAs substrates [7], and $\sigma<0$ (R<0) is a compressive film stress. The adhesion characteristics of the films were monitored using optical microscopy and the surface roughness was monitored using atomic force microscopy (AFM).

The quality of the passivation was characterized at room temperature using in-situ and ex-situ photoluminescence (PL) excited by 488 nm wavelength light from an Ar-ion laser. The in-situ PL was obtained using an optical fiber to illuminate the sample with a spot-size diameter of 0.2-0.3 cm. The accuracy of this area was limited by the spread of the beam from the end of the optical fiber, and therefore the accuracy of the power density was limited also. The emitted PL light was transmitted via the optical fiber to a monochromator with a 150 groove/mm grating and detected with a thermoelectrically-cooled CCD area-array photodetector. The power density for the in-situ illumination was approximately 200 mW/cm^2, and the power density for in-air illumination was 7 W/cm^2. Also, the leakage current and breakdown voltage were determined from the I-V characteristics of MIS structures fabricated from several of the samples.

RESULTS AND DISCUSSION

In the same manner that yielded the best results for Si substrates, ECR films grown without an applied bias on GaAs and InSb substrates at 200°C exhibited drastic differences in adhesion. Optical microscopy of the unbiased samples showed good adhesion in air and in acetone for SiN_x grown on GaAs, but in a few cases de-adhesion occurred during further device processing (e.g., spin-on resist and patterning for MIS structures). In contrast, each SiN_x film grown on InSb de-adhered from the substrate in air or acetone. The difference in adhesion can be attributed to a difference in the bond strength at the substrate-SiN_x interface for these two substrates, and therefore a difference in ability to withstand the stress in the film. The magnitude of the formation enthalpy for InN (-2.1 kcal/g-atom) is 50% less than that for forming InSb and an order of magnitude less than that for Si_3N_4. Therefore, the thermodynamically favored bonding configuration at the Si_3N_4-InSb interface is unfavorable for adhesion and alternative approaches were investigated to decrease the film stress.

Films of SiN_x were made with different compositions (from x=0.7 to x=1.8) and different thicknesses (from 38 nm to 144 nm), but the stress level was found to be relatively independent of the composition and thickness. Instead, the major effect on film stress resulted from biasing the sample during growth. Figure 1 shows the measured stresses from ECR samples grown at 250°C as a function of bias (ion energy). The energetic ion irradiation during the growth of SiN_x on GaAs decreased the high level of compressive stress in these films, and the remainder of this paper will give a more detailed characterization of these films.

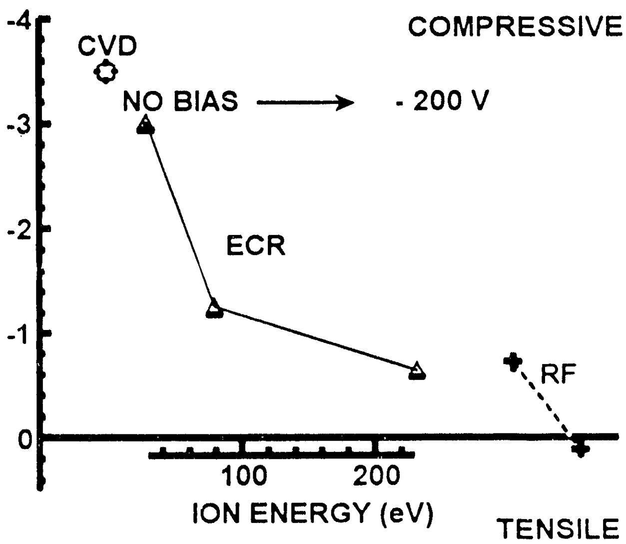

Fig. 1. The film stress for ECR-grown SiN_x (Δ) decreased as a function of applied bias. The ion energy scale is given for only the ECR plasma. The stress levels for ion-irradiated CVD [4] SiN_x (O) and RF-plasma grown [8] SiN_x (+) are shown for comparison.

For comparison to the ECR-grown films, the stress levels of CVD- and RF-plasma grown films is also shown in Fig. 1. Claassen et al. [8] demonstrated that the film stress in a plasma-deposited nitride can vary considerably depending on the growth pressure, growth temperature, and the plasma frequency. Two data points for RF-plasma films are shown in this figure in order to demonstrate this variation in stress for RF films (from compressive to tensile stress, dashed line). The RF-film exhibiting compressive stress [8] was grown on Si at a pressure of 975 mT, a temperature of 300°C, and at a frequency of 310 kHz. The RF-film exhibiting a small tensile stress is from our measurements using 13.56 MHz frequency at a growth temperature of 250°C on GaAs and a pressure of 900 mT. The data point, (O), from reference [4] was for atmospheric-pressure CVD silicon nitrides grown at 750°C on Si. The as-grown CVD films exhibited large tensile stresses. Subsequent irradiation at room temperature up to a damage level of 1 dpa caused the stress to saturate at -3500 MPa (compressive), as shown. The amount of damage in the 100 nm thick ECR film grown at a -200 V bias was estimated using the low-energy TRIM code of Brice [9] (neglecting the effects of temperature and atomic rearrangements during growth) as $\geq$ 1.9 dpa in each successive 2.5 nm layer of growth. A comparison of the stress in post-growth irradiated CVD films with the stress in ECR-films grown under biased conditions shows that the mechanism for reducing compressive stress by ion irradiation during growth is clearly different from the post-growth irradiation mechanism which increased the compressive stress. Note, if the stress level must be large, then compressive stresses are preferable to tensile stresses which may cause cracking of the SiN_x film.

Results from AFM showed a three-fold increase in surface roughness for samples grown with a -100 V bias in comparison to samples grown without an applied bias. The average rms surface roughness for a sample grown without an applied bias was 0.78 $\pm$ 0.35 nm whereas the average rms roughness for a sample grown with a -100 V bias was 2.54 $\pm$ 0.32 nm. Ion-beam analysis of the ECR-grown films, however, did not reveal intermixing between SiN_x and GaAs when the films were grown without an applied bias, with a -50 V DC bias, or with a -100 V DC bias. Furthermore, Fig. 2 shows RBS spectra from the 100 nm thick samples grown without a bias (dashed line) and with an applied bias of -200 V (solid line). For the sample biased to -200 V, the initial 5 nm of SiN_x near the substrate was grown without a bias because it was thought that this two step process would minimize substrate damage. However, the GaAs substrate did intermix with the passivation layer when the sample was biased to -200 V during growth, and this layer had a linear composition profile which varied from $Ga_{0.3}As_{0.3}Si_{0.16}N_{0.24}$ (60% GaAs: 40% $Si_{2.7}N_4$) at the interface to 100% $Si_{2.7}N_4$ at the surface. For the other samples, which exhibited no intermixing, the film compositions increased in N content with the application of a bias. For example, when all other parameters were held constant, x for the unbiased Si rich SiN_x increased from 0.92 to 1.46 by the application of a -100 V bias.

The sample grown at a bias of -200 V had the lowest level of compressive stress but it also had the smallest PL signal (dashed line in Fig. 3), which was 6 times smaller than the PL signal from the cleaned GaAs substrate in vacuum before the nitride growth (solid line in Fig. 3). All of the photoluminescence results from the samples grown with an applied bias are summarized in Fig. 4 which indicates the relative quality of the passivation layers. The largest PL signal in this figure was from the sample passivated by a SiN_x layer grown without a bias (more than twice the PL signal of the cleaned GaAs substrate). The samples grown with a bias either had little effect or had a negative effect on enhancing the PL signal in comparison to the cleaned GaAs substrate in vacuum. However, the SiN_x layers were successful in forming a chemically stable layer which protected the GaAs from air oxidation. This oxidation under laser illumination decreased the PL signal of the unpassivated substrate whereas the PL signals from the passivated samples remained constant. Another measure of the electrical quality was given by the leakage current (I_l) and

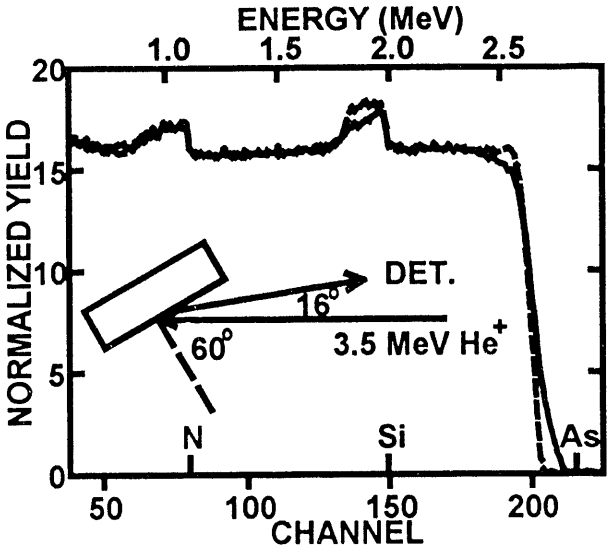

Fig. 2. RBS spectra for 3.5 MeV He^+ incident at an angle of 60° on 100 nm thick SiN_x on GaAs. The solid line is from the sample grown with a bias of -200 V and the dashed line is from the sample grown without a bias. The surface edge positions for N, Si and As are as indicated.

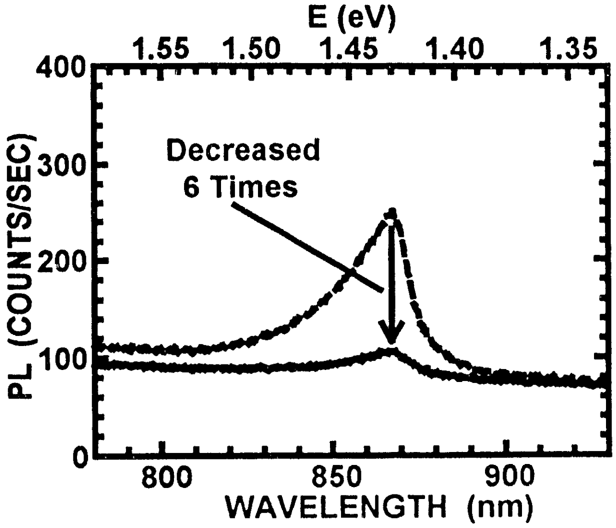

Fig. 3. Room-temperature photoluminescence (PL) measurements from the sample grown with a bias of -200 V is shown by the solid line and the signal from the cleaned GaAs substrate (in vacuum) before SiN_x growth is shown by the dashed line.

breakdown voltage (V_B) of MIS devices made from samples grown without a bias. Typically, these MIS devices had high V_B (> 9 MV/cm) and low I_l (< 3×10^{-7} A/cm^2 at $\pm$ 20 V).

The hydrogen content of the ECR films grown on GaAs decreased with increasing growth temperature, which agrees with our results for films grown on Si with compositions from Si_3N_4 to $Si_{2.7}N_4$. Growth temperatures near 50°C yielded films containing 18 at. %H for the unbiased samples, and slightly higher H contents for biased samples. Growth temperatures of 200-250°C yielded films containing 8-11 at. %H for unbiased samples and 16 %H for biased samples. Also, the variation in H concentration corresponded to deviations from the stoichiometry. Stoichiometric Si_3N_4 samples had the lowest H contents, N-rich samples had slightly higher H contents, and Si-rich samples had the highest H content. In previous work [10], a model was developed to describe the thermal release of H from SiN_x on Si; and in an effort to release H and cause relaxation of these amorphous films, the samples grown without a bias were annealed at temperatures from 400°C to 800°C. Despite some loss of hydrogen, the annealed films showed little change in compressive stress. In fact, the samples which lost the most hydrogen showed a tendency to have a slightly higher stress, but also a greatly enhanced PL signal. The best ECR-passivating-layers on GaAs were

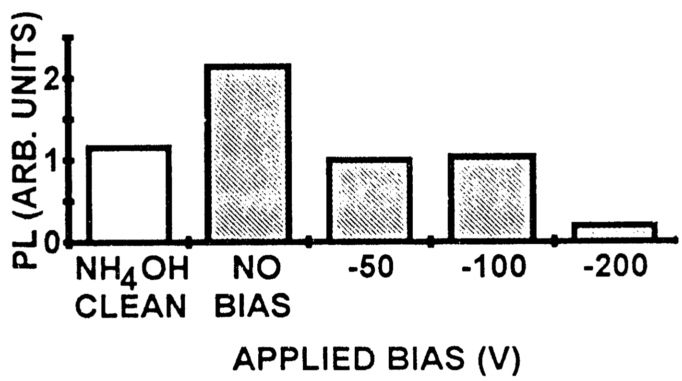

Fig. 4. A summary of passivation quality as a result of biasing the sample during growth is given by the strength of the PL signal.

the SiN_x films grown without an applied bias but annealed for short times at 800°C. This increase in PL suggests that interface states or centers of non-radiative recombination in bulk GaAs are being effectively passivated by the release of H from SiN_x.

CONCLUSIONS

This work has demonstrated that ECR-Si_3N_4 films grown at temperatures from 35°C to 250°C on GaAs and InSb substrates are under a high state of stress when the sample is electrically isolated during growth, which may lead to de-adhesion from the substrate. The problem of de-adhesion was found to be particularly severe when the samples were processed further for device applications. The high compressive stress on GaAs was reduced to a small compressive stress by negatively biasing the sample and thereby causing energetic ion irradiation during growth. However, an applied bias of -200 V (ion energy $\approx$ 230 eV) caused the GaAs substrate to intermix with the SiN_x layer. The results showing a decrease in stress, as a result of energetic ion growth, suggest that a bias can be applied half-way into the growth process of thick films such that the thickness of the first half of the layer is sufficient to impede interface mixing, yet still attain much of the favorable reduction in stress. Photoluminescence was used as a measure of the passivation quality and the samples grown with an applied bias had a reduced PL signal as compared to the sample grown without an applied bias. The sample grown without an applied bias had twice the PL signal of a cleaned GaAs substrate in vacuum. Further, samples grown without an applied bias were annealed in an effort to release H, relax the amorphous film, and reduce the level of stress; but instead, annealing caused a slight increase in the film stress. Never-the-less, the best ECR passivation layers (as determined from PL measurements) were obtained for those films where H was released and could passivate non-radiative recombination centers.

REFERENCES and ACKNOWLEDGMENTS

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