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Physical and electrical characterisation of oxynitride films produced by plasma oxidation of deposited silicon nitride layers

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LPCVD silicon nitride films have been oxidised in an oxygen plasma using low thermal budget plasma anodisation to produce oxynitride films. The electrical integrity of these films was generally shown to improve following oxidation and a model of the conduction processes in the oxynitride has been suggested.

1. INTRODUCTION

Interest in polysilicon and/or amorphous silicon Thin Film Transistors (TFT's) for large area active matrix LCDs is currently very high since the potential market for such displays is enormous. An essential requirement for the TFTs in the matrix is a low thermal budget dielectric with good electrical integrity and a commonly used dielectric is silicon nitride fabricated by LPCVD or PECVD. Previous work considered the plasma oxidation of PECVD nitride [1]. We investigate here the physical and electrical properties of novel oxynitride films prepared by low temperature (430°C) inductively coupled RF plasma oxidation of LPCVD silicon nitride deposited on single crystal silicon.

2. EXPERIMENTAL

The substrates used in this investigation were RCA cleaned, 5 inch <100> silicon wafers Boron doped to $5 \times 10^{14} \text{ cm}^{-3}$. LPCVD nitride films were then deposited to thicknesses of 20 and 50 nm. The plasma oxidation reactor was of the inverted type and has been described elsewhere [2]. This was used to anodise the nitride films in an oxygen plasma using an incident rf power of 0.6 kW, a d.c. bias of 150 V, process pressure and temperature were 150 mTorr and 430°C respectively. Only the central area of the nitride film was exposed to the oxygen plasma for times ranging from 10-40 mins. Following plasma processing an array of MIS capacitors was formed by the evaporation of 200 nm of high purity aluminium through a shadow mask. Capacitors were formed both on the nitride and oxynitride areas.

2.1 Electrical characterisation

Electrical properties were investigated using high and low frequency CV and IV measurements prior to and following Post Metallisation Annealing (PMA) in forming gas. By varying the plasma oxidation conditions the overall refractive index (n_i) and the corresponding dielectric permittivity (ϵ_i) of the resultant film was adjustable between 2.0 to 1.43 and 6.9 to 3.7 respectively corresponding to (almost) pure nitride to oxide. The electrical integrity of the nitride films was generally found to improve with oxidation and a summary of these results for three representative samples (155, 156 and 157) is shown in Table 1 where C_i refers to the MIS accumulation capacitance. A marked reduction in midgap interface trap density (D_{it}) following plasma oxidation of the nitride film and PMA is possible. Oxide fixed charge (N_f) determined from the flatband voltage shift during high frequency CV remains largely unaffected. Breakdown strength improved by as much as 30% following anodisation.

Table 1: Table of physical and electrical parameters of the nitride and resultant oxynitride

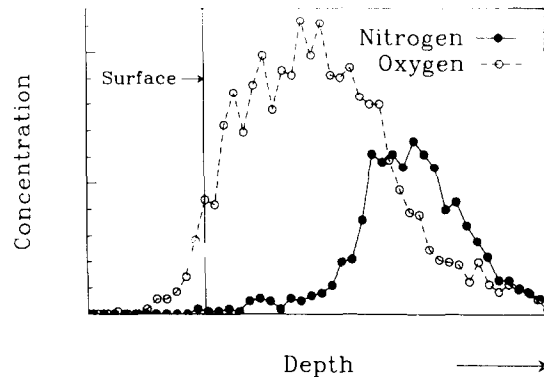
	Nitride		Oxynitride	
	As deposited	After PMA	As grown	After PMA
Sample	155			
Depth (nm)	22.0	22.0	68.5	72.0
C_i (pF)	309.3	290.3	63.1	51.9
ϵ_i	6.8	6.4	4.3	3.7
n_i	1.93	1.93	1.43	1.46
N_f ($\times 10^{11} \text{ cm}^{-2}$)	17.3	12.7	30.0	6.4
D_{it} ($\times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$)	214	244	-	0.6
Sample	156			
Depth (nm)	21.0	21.0	25.0	25.0
C_i (pF)	306.8	329.8	188	205
ϵ_i	6.4	6.9	4.7	5.1
n_i	1.93	1.93	1.63	1.63
N_f ($\times 10^{11} \text{ cm}^{-2}$)	48.0	21.0	55.2	16.3
D_{it} ($\times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$)	-	-	-	61.7
Sample	157			
Depth (nm)	49.0	49.0	66.5	69.5
C_i (pF)	120.6	124.5	58.3	60.4
ϵ_i	5.9	6.1	3.9	4.2
n_i	2.0	2.0	1.55	1.53
N_f ($\times 10^{11} \text{ cm}^{-2}$)	24.7	26.2	55.8	21.1
D_{it} ($\times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$)	-	-	372	0.4

2.2 Physical characterisation

Physical properties were investigated using ellipsometry, Transmission Electron Microscopy (TEM), Auger Electron Spectroscopy (AES), and Elastic Recoil Detection (ERD). Cross sectional TEM results following oxidation of the nitride reveal the presence of an oxygen rich surface layer which increases in thickness as oxidation proceeds, confirming earlier work on plasma oxides [3]. AES also shows the presence of this top layer and reveals an enhanced concentration of oxygen at the Si-oxynitride interface compared to the nitride case. The ERD technique is complementary to Rutherford Backscattering Spectrometry (RBS) and allows the detection of light elements (H,C,N,O) in heavier

matrices. ERD confirmed the above results and a typical spectrum is shown in figure 1 with a summary of the O,N and H areal density for the oxynitride films shown in table 2. From these results it would appear that the oxidation proceeds by the substitution of excited oxygen species from the plasma for nitrogen atoms in the silicon nitride network, a process which proceeds from the surface towards the Si-oxynitride interface and can result in conversion of the entire nitride film to silicon dioxide for long anodisation times (e.g. sample 155). In addition there is some inward migration of oxygen species towards the Si-oxynitride interface which has the effect of reducing the interface state density.

Figure 1 ERD depth profile of the oxynitride sample 156 after PMA (Concentration in arbitrary units, film thickness 25nm)



The hydrogen content of the oxynitride films remains roughly the same (within a factor of 2) following PMA even though the D_{it} is reduced indicating that the effect of the PMA is to redistribute hydrogen and passivate dangling bonds rather than introduce significant new amounts of hydrogen.

Table 2: Table of oxygen, nitrogen and hydrogen areal densities following PMA obtained from samples 155, 156 and 157 using ERD.

Sample	Oxygen (*10 ¹⁷ cm ⁻²)	Nitrogen (*10 ¹⁷ cm ⁻²)	Hydrogen (*10 ¹⁷ cm ⁻²)
155	4.8	0.003	0.18
156	2.9	1.1	0.18
157	0.99	0.6	0.10

2.3 Electronic conduction in the films

Figure 2 shows electronic conduction through the nitride films which was found to be independent of the injecting electrode and well described by the Poole-Frenkel (P-F) mechanism with a trap depth of 0.821 eV. Current density through the plasma oxidised nitride (oxynitride) was found to be much lower at a given field and also to be dependent upon the material of the injecting electrode. For high fields ($E > 8$ MV/cm) conduction through the oxynitride could be described by Fowler-Nordheim (F-N) tunneling from the silicon with a barrier height of 2.8 eV into the dielectric and assuming an electron effective mass of $m_{ox} = 0.5m_0$. At lower fields ($5 < E < 7$ MV/cm) both P-F and F-N models are inadequate to describe the conduction process in the oxynitride and following Yang et al [4] we postulate electron tunneling to and subsequent re-emission of electrons from shallow traps in the dielectric to the oxynitride conduction band according to:

$$J = f(N_{sh}) E^2 \exp(\beta \Phi_{sh}^{3/2}/E)$$

where N_{sh} and Φ_{sh} are the density and trap depth of the shallow traps respectively, and

$\beta = (8\pi/3qh)(2m_{ox})$ where h is Planck's constant and q the electronic charge. At intermediate fields (7-8 MV/cm) electrons are able to tunnel to deeper traps in the dielectric and be retained and this is responsible for the ledge in the J-E plot. Thus following plasma oxidation it appears that traps in the silicon nitride are either annealed (since bulk trap density in the oxynitride $\ll$ bulk trap density in the nitride) or transformed to deeper traps in the resulting oxynitride.

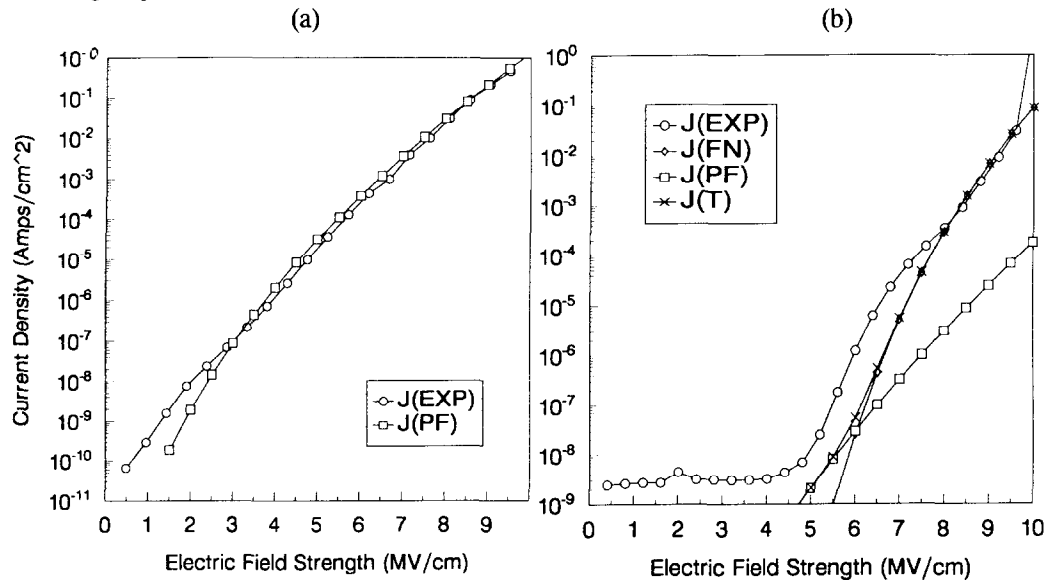


Figure 2 J versus E plots for the films showing the experimental curves (J_{EXP}) with those plotted using Fowler-Nordheim (J_{FN}) and Poole-Frenkel (J_{PF}) expressions and their sum (J_T) for (a) nitride (b) oxynitride

3. CONCLUSIONS

A low thermal budget oxynitride has been realised using plasma oxidation of LPCVD (or PECVD) silicon nitride at 430°C. Such a dielectric could have useful application in TFT production for display technology where the use of high temperatures is precluded. By varying the plasma oxidation conditions the overall refractive index (n_i) of the resultant film can be adjusted between 2.0 and 1.43 and the dielectric permittivity (ϵ_i) correspondingly varied between 6.9 and 3.7. The process is thought to occur by $=N/=O$ exchange at the plasma-dielectric interface though some migration of oxygen species, possibly field assisted during the oxidation, does occur and this both increases the barrier height and passivates the Si-oxynitride interface. Following oxidation therefore the electrical integrity generally improves in that D_{it} and leakage current are reduced and breakdown strength increased.

REFERENCES

1. R. Goswami, J.B. Butcher, R. Ginige, J.F. Zhang, S. Taylor, and W. Eccleston, *Electron. Lett.*, 24 (1988) 1269.
2. G.P. Kennedy, S. Taylor, W. Eccleston, and M.J. Uren, *Microelectron. J.*, 25 (1994) 485.
3. S. Taylor, S., W. Eccleston, J. Ringnalda, D.M. Maher, D.J. Eaglesham and C.J. Humphreys, *J. de Physique*, C4 (1988) 393.
4. B.L. Yang, H. Wong and Y.C. Cheng, *Solid State Electronics*, 37 (1994) 481.