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Liquid phase deposited SiO_2 on GaN

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Abstract

An efficient and low cost approach to deposit uniform silicon dioxide layers on GaN by liquid phase deposition (LPD) near room temperature are described and discussed. The process is simple. GaN wafers are immersed into a H_2SiF_6 and H_3BO_3 solution to form the silicon dioxide layers. The deposition conditions and the properties of the SiO_2 films will be characterized.
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Keywords: Liquid phase deposition; Silicon dioxide

1. Introduction

Recently, research on GaN-based materials has attracted not only its use in the light emitting devices, but also in the power applications. The GaN-based FETs are attractive in power amplification and switching under high power and high temperature application [1,2]. This is due to the wide band gap (3.4 eV), high breakdown voltage ($>5 \times 10^6$ V cm^{-1}), unique chemical and thermal stability possessed by GaN. Although GaN FETs and AlGaN/GaN heterostructure FETs have been reported [3–5], the Schottky gate barrier still limits the swing voltage and gate leakage which can be solved by metal-oxide-semiconductor(MOS) structures. Efforts have been made in pursuit of high quality gate insulators, such as SiO_2, Si_3N_4 etc. [6,7], and photoanodic oxide have been developed [8]. The reliable oxide (insulator) layers on GaN, however, are very few reported to be seen on GaN MOSFET. Recently, Ren et al. [9,10] reported using e-beam evaporation in a molecular beam epitaxy (MBE) chamber to deposit Ga_2O_3 (Gd_2O_3) as the gate dielectrics for GaN MOSFET. However, the required systems and procedures are complicated.

Liquid phase deposition (LPD) process, a low temperature, low cost and reliable method, has been used to deposit high quality insulators on Si and GaAs material system with promising results [11]. However, its exploration to GaN materials is not developed. In this work, LPD process will be employed for the insulating dielectrics on GaN with the supersaturated hydrofluosilicic acid (H_2SiF_6) and the boric acid (H_3BO_3) aqueous solution. The properties of the oxide films will be characterized. The selective deposition on GaN, photoresistor, and metals will also be described.

2. Experimental

The experimental setup for preparing LPD silicon oxide is shown in Fig. 1, it only consists of a temperature controller, substrate holder in the saturated solution. The preparation of the saturated solution and the depositing flowchart is illustrated in Fig. 2. The GaN samples, grown on *c*-plane sapphire substrates, were all prepared by MOCVD. The LPD technique utilizes supersaturated hydrofluosilicic acid aqueous solution (H_2SiF_6) as a source liquid and boric acid aqueous solution (H_3BO_3) as a deposition rate controller. The chemical reaction in the aqueous solutions of hexafluorosilicic acid (H_2SiF_6) can be expressed in the following.

$$\Delta H + H_2SiF_6 + 2H_2O \leftrightarrow 6HF + SiO_2 \downarrow \qquad (1)$$

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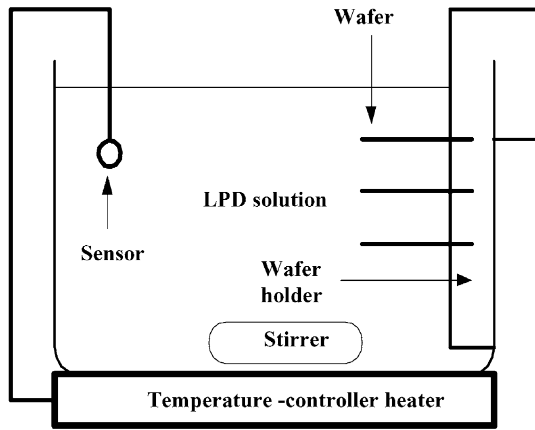
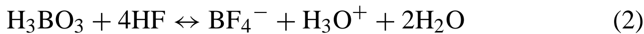


Fig. 1. The setup of the LPD system.

When the aqueous solution of boric acid (H_3BO_3) is dipped into the solution, H_3BO_3 reacts with HF and they generate boron tetrafluoride ions (BF_4^-). The chemical reaction is shown in the following.



$$H_3BO_3 + 4HF \leftrightarrow BF_4^- + H_3O^+ + 2H_2O \quad (2)$$

While a wafer is dipped into a HF solution saturated by SiO_2, the chemical reaction of Eq. (1) is in a balanced condition. The addition of H_3BO_3 consumes HF through the reaction of Eq. (2) and reduces the concentration of HF solution in Eq. (1). The reduction of HF in dipping solution will shift the equilibrium to the right of reaction (1). Therefore, addition of H_3BO_3 shifts the equilibrium to the deposition of SiO_2 on substrates. The mechanism is similar to that of SiO_2 on Si.

The chemical composition of silicon oxide was studied by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). The depth profile of oxide films was performed by secondary ion mass spectrometer (SIMS). Surface morphology of selective LPD oxidation on GaN was investigated by scanning electron microscope (SEM) and atomic force microscope (AFM).

Electrical properties of the SiO_2 layers on MOS structures were characterized by HP4280A and HP4156B for capacitance–voltage (C–V) and current–voltage (I–V) measurements. The LPD-silicon oxide films worked as the insulator and Al metal gates were evaporated through a shadow mask. Ohmic contact to the n-GaN was Ti/Al/Au (25/100/100 nm). Photo-enhanced chemical etching performs the device isolation.

3. Results and discussion

Fig. 3 shows the deposition rate of SiO_2 on GaN at 40 °C [12] with the concentration of H_2SiF_6 and H_3BO_3 at 0.4 and 0.01 M, respectively. Also shown is the deposition rate on GaAs for comparison. Due to the transparency of the GaN substrate to He-Ne laser, thickness of the oxide was determined by Dektak through the selective deposition of oxides on photoresistor instead of by Ellipsometer as appeared in GaAs. The thickness of the oxide was consistent with those measured by SEM. The oxidation rate is about 50 nm h^{-1}. There is almost no difference between the deposition rate on GaN and that of GaAs. The LPD-silicon oxide deposition rate first increases with H_3BO_3 concentration, and then becomes saturated. After reaching a maximum, the deposition rate decreases again. This is explained by the variation of pH values, and the role of H_3BO_3, as shown in the figure. The increase of pH value from −0.38 (starting solution), −0.09

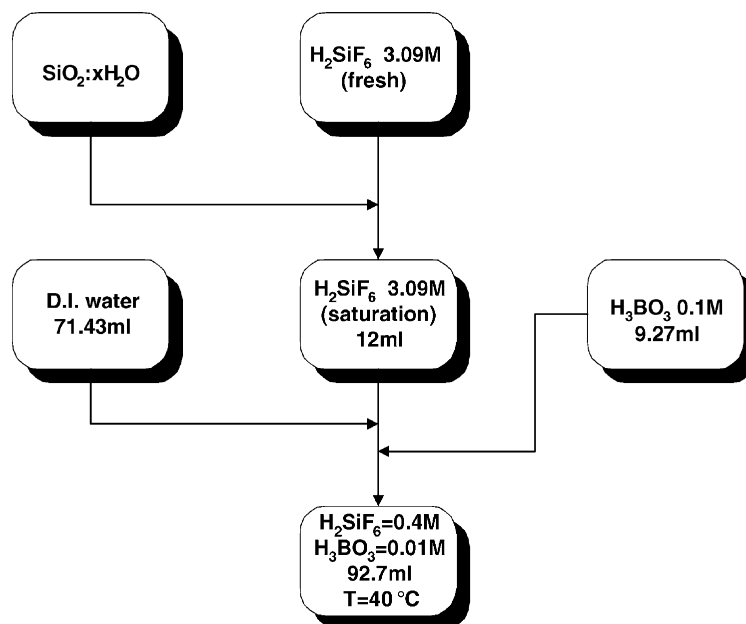


Fig. 2. The flowchart for depositing SiO_2 films on GaN layers.

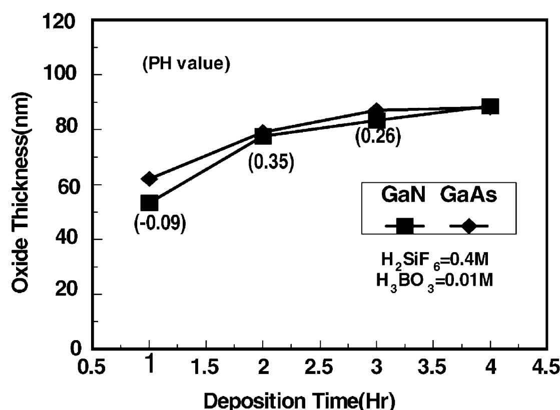


Fig. 3. SiO_2 deposition rate on GaN and GaAs as a function of time.

to 0.35 marks the reaction of Eq. (1) to suit the SiO_2 deposition. At the third hour, the pH value decreases to 0.26 and the thickness of the oxide is almost kept constant. It means that the reaction is balanced, for example, the deposition rate is equal to the etching back rate. After this, the etching rate is larger than that of deposition, resulting in the decrease of oxide thickness. By adding H_3BO_3 to adjust the pH value, constant deposition rate is obtained. Otherwise, etchback is to be observed. The growth solution becomes turbid if large amount of H_3BO_3 is added into an extremely low H_2SiF_6 concentration [13,14].

Typical Fourier transform infrared spectroscopy spectra ranging from 400 to 1400 cm^{-1} deposited LPD-SiO_2 films on GaN; Si and GaAs (100) substrates are shown in Fig. 4. The transmission bands are almost the same. The peaks around 455, 810 and 1090 cm^{-1} are attributed to Si–O rocking, Si–O bending and Si–O stretching vibration, respectively. The LPD-SiO_2 film is abundant in Si–O–Si bonds and has an orderly silica network and consequently good chemical stability. Another main transmission band around 935 cm^{-1} is found in the LPD-SiO_2 spectra and may be attributed to Si–F stretching vibration. The fluorine (F) contained in the Si–F bond must be incorporated from the H_2SiF_6 solution. The oxide perhaps is more accurate to be considered as SiOF instead of SiO_2. However, as the result of secondary ion mass spectrometer depth profiles and the Auger analysis, F is not found in SiO_2 on GaN due to detection limitation.

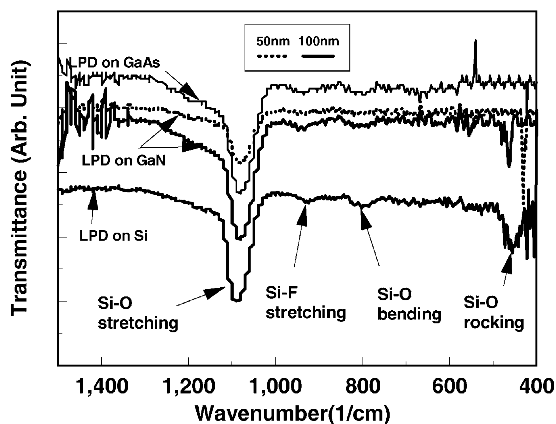


Fig. 4. FTIR spectra for 50 and 100 nm thick SiO_2 on GaN. Also shown are the LPD-SiO_2 on Si and GaAs substrates for comparison.

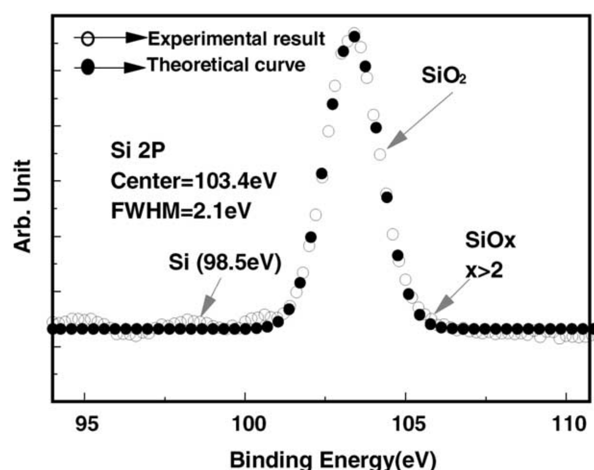


Fig. 5. The XPS data of Si 2p core level of LPD-SiO_2 on GaN substrate prepared at $T = 40\,^{\circ}C$. Also shown is the theoretical fitting curve for comparison.

XPS was performed with a Mg Kα X-ray source. The electron analyzer normal collects Si 2p, C 1s, and O 1s core levels to the surface. Fig. 5 shows the Si–O bonding spectra fitting to the Gaussian distribution function. The Si 2p line through SiO_2/GaN is separated into three species, that is, elemental Si (binding energy: 98.5 eV), the oxidized Si (SiO_2) (103.4 eV, FWHM: 2.1 eV) and SiO_x. As the results show, the composition of the oxide films might then be attributed to SiO_2.

Fig. 6 shows the surface morphologies of the oxides on GaN and Al-metal. Smooth oxide surface can be seen only on GaN. This provides potential device applications. Also shown in Fig. 6(b) is the AFM analysis for a 70 nm thick oxide. The root mean square (RMS) surface roughness is 5.2 nm, which is high as compared to the SiO_2 on Si (0.2 nm). Similar work is also seen on GaAs surface which is perhaps due to the polar substrate.

As shown in Fig. 7, the typical LPD-SiO_2 on GaN breakdown field for various thickness of oxide of 50, 70, 85 and 100 nm are 3.42, 3.8, 5.1 and 7 MV cm^{-1}, respectively. It also shows the comparison of LPD-SiO_2 on GaAs and Si at thickness of 27 and 24 nm, respectively. The carrier transports deduced from the log I versus $V^{0.5}$ for low and high electrical field corresponded to the Schottky emission and Poole–Frenkel conduction, respectively. At an electric field of 1 MV cm^{-1}, the corresponding leakage current densities ranged from 10^{-4} to 10^{-5} A cm^{-2}, which are higher than those on GaAs or Si wafers. This is in consistence with the rougher surface of SiO_2 on GaN layer. After annealing oxide at 900 °C in N_2O for 20 min, the leakage current densities can be lowered to less than 10^{-7} A cm^{-2}.

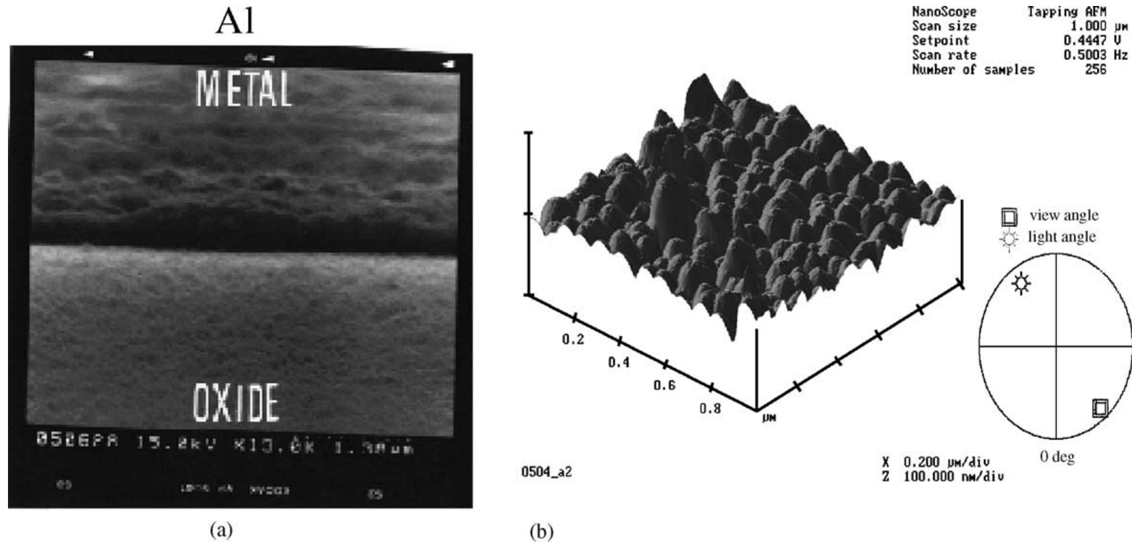


Fig. 6. The SEM photograph and AFM 3-D image of LPD oxide surface (a) The smooth selective LPD oxide surface on GaN. (b) The AFM surface morphology on a 70 nm thick oxide with a RMS roughness value of 5.2 nm.

The typical *C–V* characteristics measured by 4280 A at 1 MHz are shown in Fig. 8. The deduced interface trap density with $2.8 \times 10^{11}\,cm^{-2}\,eV^{-1}$ for an oxide thickness of 50 nm on GaN can be obtained [15]. After annealing oxide at 900 °C in N_2O for 20 min, the interface trap density can be lowered to less than $1.9. \times 10^{11}\,cm^{-2}\,eV^{-1}$. It also indicates that the interface trap density is further reduced to less than $10^{11}\,cm^{-2}\,eV^{-1}$upon suitable annealing processes. However, there is still much room to improve the film quality as compared to SiO_2/Si interface. Although the properties of SiO_2 on GaN are not as good as those on Si or GaAs, however, it remains fine for device applications. Details of the LPD oxide gated GaN MOSFETs and AlGaN/GaN heterostructure MOSFETs are seen elsewhere [16,17].

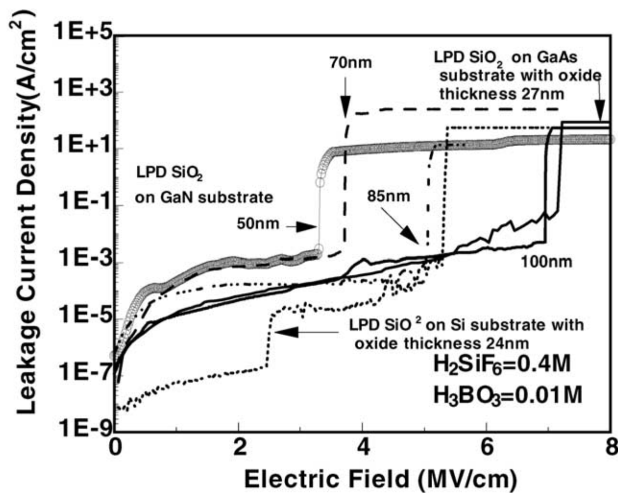


Fig. 7. The log *I–V* characteristics for the 50, 70, 85 and 100 nm thick SiO_2 on GaN. Also shown are the SiO_2 on Si and GaAs substrates for comparison.

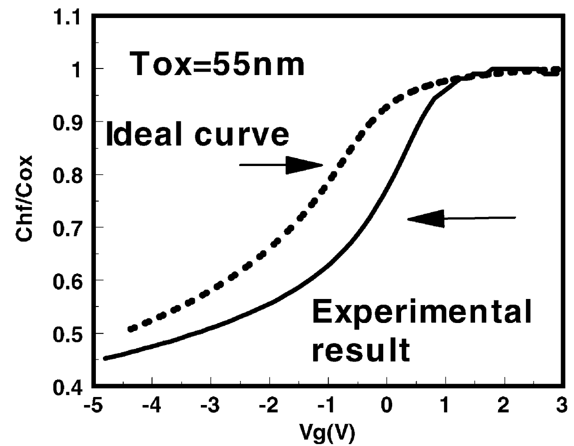


Fig. 8. The measured and ideal *C–V* characteristic for a 50 nm thick LPD-SiO_2 on GaN MOS diode. The deduced interface state density is about $2.8 \times 10^{11}\,cm^{-2}\,eV^{-1}$.

4. Conclusion

The liquid phase deposited SiO_2 on GaN surface has been demonstrated and characterized. The leakage current, breakdown field and interface trap has also been discussed. As the results show, the proposed method is likely to have the potential for device application.

Acknowledgements

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