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$_2$SiF$_6$ and H$_3$BO$_3$ solution to form the silicon dioxide layers. The deposition conditions and the properties of the SiO$_2$ films will be characterized.

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), 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$_3$N$_4$, 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$_2$O$_3$ (Ga$_2$O$_3$) 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$_2$SiF$_6$) and the boric acid (H$_3$BO$_3$) 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$_2$SiF$_6$) as a source liquid and boric acid aqueous solution (H$_3$BO$_3$) as a deposition rate controller. The chemical reaction in the aqueous solutions of hexafluorosilicic acid (H$_4$SiF$_6$) can be expressed in the following.

$$\Delta \left. \Delta H \right|_{\text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \leftrightarrow 6\text{HF} + \text{SiO}_2} = (1)$$
When the aqueous solution of boric acid (H$_3$BO$_3$) is dipped into the solution, H$_3$BO$_3$ reacts with HF and they generate boron tetrafluoride ions (BF$_4^-$). The chemical reaction is shown in the following.

$$\text{H}_3\text{BO}_3 + 4\text{HF} \leftrightarrow \text{BF}_4^- + \text{H}_3\text{O}^+ + 2\text{H}_2\text{O} \quad (2)$$

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$_3$BO$_3$ 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$_3$BO$_3$ 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$_2$SiF$_6$ and H$_3$BO$_3$ 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 photoreistor 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$_3$BO$_3$ 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$_3$BO$_3$, as shown in the figure. The increase of pH value from −0.38 (starting solution), −0.09
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$_3$BO$_3$ 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$_2$SiF$_6$ is added into an extremely low H$_2$SiF$_6$ 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$_2$SiF$_6$ 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.

XPS was performed with a Mg K$_\alpha$/H$_9251$ 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$_2$.

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 $10^{-7}$ 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$_2$O 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 $2.8 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1}$ for an oxide thickness of 50 nm on GaN can be obtained [15]. After annealing oxide at 900 °C in N$_2$O for 20 min, the interface trap density can be lowered to less than $1.9 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1}$. It also indicates that the interface trap density is further reduced to less than $10^{11} \text{cm}^{-2}\text{eV}^{-1}$ 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 50nm thick LPD-SiO$_2$ on GaN MOS diode. The deduced interface state density is about $2.8 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1}$.

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.

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