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The Effect of GaN Nanostructure Layers on the Toxic Gas Sensor Sensitivity

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Abstract: In this paper, ammonia gas sensor based on Ag/GaN/ Si and Ag/GaN/PS with (3 and 7 layers) was fabricated; the effect of number of layers on the morphology, structural, and sensitivity of the device has been studied. XRD pattern for GaN/Si showed that the film has a polycrystalline structure in nature with presents many of diffraction peaks of hexagonal structure, with the exception of plane (111) at 39.09 which has a cubic structure, no other structures such as Ga2O3 is found, and these indicates that GaN output from the precursor was highly successful. FESEM images showed a change in surface morphology as the number of layers increases. from AFM technique, it's found that reduced in particle size can significantly affect sensitivity improvement, therefore the maximum sensitivity to NH3 gas was observed in GaN/PS (3 layers) which possess the few grain size, and found to be 931 %, at 100ºC.

Keywords: Effect, GaN, Spin coating, Porous Silicon, Hexagonal phase

INTRODUCTIOIN

III-Nitrides semiconductors such as GaN, AlN, and InN are the materials that attract attention because they have many good properties such as high temperature stability, high electronic saturation speed and high direct energy gaps [1]. Nitride-III group transitional direct energy gap ranges from 1.9 (InN) to -6.2 eV for (AIN) [2]. Among the (III-Natride) group, Gallium Natride (GaN) has caught the attention of researchers because of its unique properties, such as has wide energy gap about 3.4 eV, high temperature stability, and strong polarization, that make it widely used in many applications like ;diode, LDS laser diodes with UV spectrum range, solar cells and gas sensors [3-5].

It has a crystalline structure of wurtzite that makes it possible to use in devices applications especially, optoelectronics, high-power and high frequency devices [6]. Due to the mentioned optical and structural properties, GaN reduces the problems that caused by generation thermal and optical of the charge carriers [7]. One of the important characteristics that made its use as a gas sensor has a deep parabolic range, which provides permissible reactions on the surface most of these reactions can significantly affect the electronic properties of the surface, such as surface states or surface curvature, and this affects the sensitive surface [8- 9].

The sensitivity can be define to gas is the ratio between the resistance of air to the resistance to the gases, Ra/Rg, where Ra the resistance of air sensors, Rg the resistance of NH3 gas [10]. In addition, the response time very important for any sensor device because it determines the time which takes for the sensor to reach 90% of the maximum / minimum value of the conduction when the gas flows and the recovery time, and the recovery time the required time to recover within 10% of the total value of the gas flowing [11].

Gas sensors called the electronic noses, which are devices that are able to capture and treatment of the signals resulting from the interaction of the surface with a specific gas. For making a good sensor, the power must be low to operate and compatible with a simple system and high sensitivity with response times less than one minute, the small sensor works very efficiently and has frequent responses. It is important that the sensors are not sensitive to the ambient temperature and the changing gases in the surrounding air.

Gas can be discovery in two ways. The first way is to detect the calories in which the high temperature is a measure of the gas concentration, the second way is the detecting the gas concentration by change sensor parameters resulting from the absorption or interaction of gases on solid surfaces, these two methods were widely

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reviewed by Grundy and Jones, through the interaction of the surface with gas, this phenomenon is called adsorption, which divided into; physical adsorption, its occurs due to the weak forces of Van der Waals[12], and chemical absorption, this type occurs due to high surface energy, the reaction is inside where the inner bonds are broken, thus changing the crystalline structure with a high temperature [13]. In 2003, Dae-Sik Lee and others studied thin film (GaN) as gas sensors, where the particles were implanted from gallium using the organic mineral chemical vapor deposition method (MOCVD) at 1030°C on the sapphire substrates, with thin Pt sedimentation on the surface and used to detect some gases, and in the end result the GaN gas sensor showed high sensitivity, high recovery, selectivity, and good recovery time[14]. In 2016 K. ELHussein et al, studied GaN thin film synthesis using a low-cost electrochemical deposition technique for hydrogen gas sensor, the I-V property of the Schottky hydrogen valve was measured at different flow rates at room temperature, it has been found that GaN deposited on Si (111) is more sensitive than the Si (100) substrate, where experimental results indicate the possibility of using GaN thin film as gas sensors[15].

Porous silicon (PSi) is good material used as substrate in many electronic and sensor applications compared to bulk materials due to the surface morphology properties, the ratio of surface to size very high, it is easy to control surface morphology by controlling the formation parameters, in addition to the optical and electronic properties [16]. One of very important way is the addition of the catalyst active metals such as platinum (pt), gold (Au), and Silver (Ag) as a contact, which enhance improves the sensitivity and rapid response of the thin film [17]. In this work, the effect of changing the number of layers of GaN/PSi and Si on the properties of NH3 gas sensor achieved.

MATERIALS AND METHODS

EXPERMINTAL PARTS

The photo- electrochemical etching (ECE) technique used to prepare PS of n-type <111> oriented silicon substrate at a resistance of 0.5 Ω. The etching cell is made of thermal Teflon. Si wafer was cut into square-shape pieces ($1cm^2$) and then anodized in a solution containing 48% HF and ethanol at 1:4 ratio. Porous silicon was prepared under illumination with halogen lamp (70Watt) and current density ($24mA/cm^2$) for 20 minute. A two-electrode system is applied, and Pt mesh used as cathode and Si as anode. Spin coating technique is used to deposit thin film of the GaN nanostructures on silicon and quartz substrates with various layers of coatings. Gallium (111) nitrate hydrate Ga(NO3)3•xH2O) powder purches from TEFIC BIOTECH CO., LIMITED, was dissolved under stirring in ethanol (CH3CH2OH) which was continued for 1 hour. To order to dissolve the metals completely during stirring, the precursor solution (0.3 M) was stirred at 50 ambient for 3 hours. The solution was then dropped onto a silicone and quartz substratum (20 mm x 20 mm x 1 mm) that rotated for 60s at 300 rpm. After the spin coating had been deposited, the thin films were dried on a hot plate for 1 hour at 100^oC. The processes of coating and drying were repeated several times to synthesize multilayer. The samples were annealing in furnace at 950oC with NH3 gas flow at ratio 6% for 1 h. The MSM device was preparation by the metallization of spacemen, the metal contacts of finger-shaped silver (Ag) electrodes of 500 nm thickness were deposited over the GaN/Si, PSi sample using an E306A Edwards thermal evaporation system. The samples, annealed under 6% of NH3 gas flow in furnace at 950°C for 1 h. X-ray diffraction (XRD) technique (Philips PW 1710 X-ray diffractometer, USA) with Cu Kα radiation utilized. The morphology of the films was examined by Field Emission Scanning Electron Microscope (FESEM) system (NOVA NANOSEM 450, USA) and AFM, SPM model AA3000. The gas sensor system consists of Laptop PC and a "PC-interfaced digital multimeter of type UNI-T UT81B" used to record the alteration in the sensor resistance when exposed to air-NH3 gas mixing ratio.

RESULTS AND DISCUSSIONS

XRD

Figure .1 showed XRD pattern of GaN thin film deposited on Si and PSi substrates with 3 and 7 layers using spin-coating technique under annealing by NH3 at 950°C. Figur1-a represent XRD peaks of GaN/Si (111) as function of number of layers, the figure showed that the film has a polycrystalline structure in nature with presens many of diffraction peaks indicating the planes (100), (002), (101), (103) and (004) of Hexagonal structure, with the exception of plane (111) at 39.09 which has a cubic structure, and this corresponds with standard data (JCPDS-01-089-7522 and 01-088-2361), may be the reason for this different plane is due to annealing via NH3 at a high temperature, which can improve the structure by reducing defects [19]. In the same figure when the number of layers increased to 7layers, an increase in the intensity of diffraction peaks occurs, due to the increasing the number of small and large nanoparticles [20].

Figure 1-b explain XRD peaks of GaN/PSi as a function of number of layers, it showed an increase in the intensity of diffraction peaks, with increase in the number of layers compared to silicon substrate, as well as the figure showed that the film has many of diffraction peaks, refer to the planes (002),(101) and (110) of hexagonal GaN, which corresponds with standard data (JCPDS- 01-079-7522 and 01-079-0622) ,this is agree with Asmiet Ramizy etc.,[21]. No other structures such as Ga2O3 is found, indicate that GaN output from the precursor was highly successful due to the complete transformation of all Ga2O3 layers into GaN.

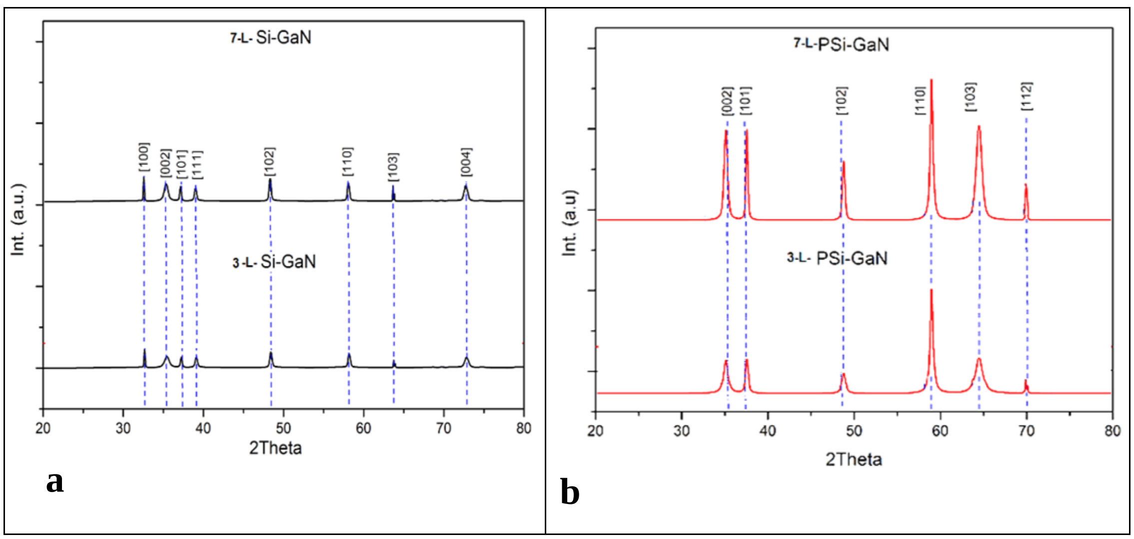


FIGURE 1.XRD of GaN with 3and 7 layer on (a) Si and (b) PSi.

The mean crystalline size (D), can be calculated from Debye-Scherrer formula [22] with aid FWHM of XRD planes.

$$\mathbf{D} = \frac{\mathbf{K\lambda}}{\boldsymbol{\beta}\mathbf{cos}\boldsymbol{\theta}} \qquad (1)$$

Where K is the Scherrer constant equal to 0.9, λ is the wavelength in nanometers, β is FWHM in radians, and θ is the diffraction angle in radians. The results display that the mean crystallite size of GaN increases when number of layer increase, and FWHM decreases, as shown in Table 1. The change in the strain of GaN crystals calculated utilizes the equation [23].

$$\zeta = \frac{\beta \cos\theta}{4} \qquad (2)$$

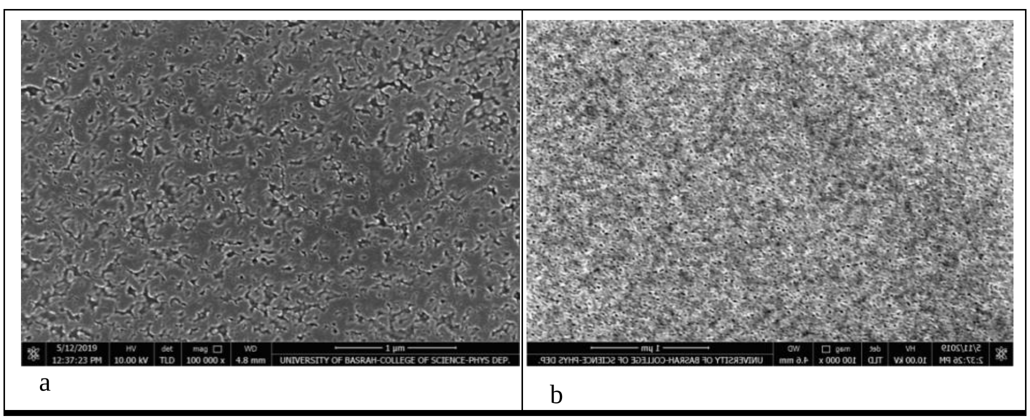
Where ζ :is the strain of thin film prepared. The strain of GaN crystal decrease with thickness increases as shown in Table 1.

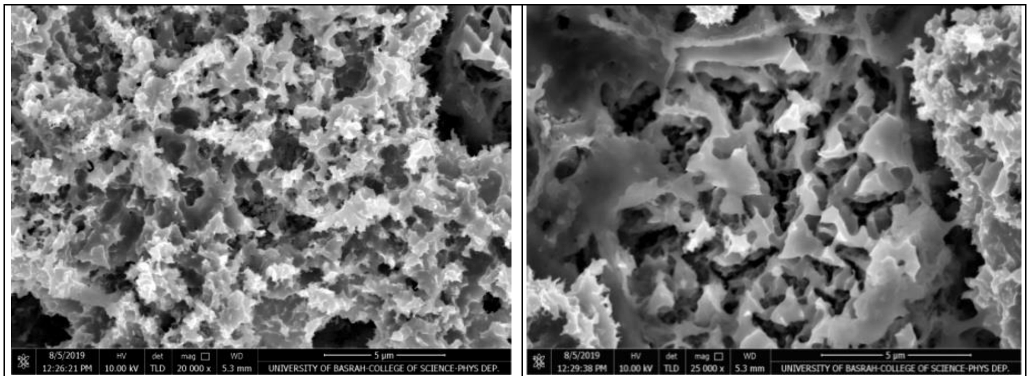
TABLE 1. The variation in the strain and crystallite size as a function of layers and substrate.

sample	substrate	Crystal size (nm)	Strain (rad)
3L	Si	29.2	0.458
7L	Si	52.0	0.21
3L	PS	15.2	0.453
7L	PS	21.5	0.423

FESEM

The images of Field Emission Scanning Electron Microscope (FESEM) for GaN thin film which deposited on different substrates, illustrated in Fig2. Fig (2-a and b) showed the FESEM image of GaN/Si with 3 and 7 layer, the film showed more smooth and homogenous and coverage all substrate compare with 7L, these agree with AFM result. The film with (7 layer) showed regularly distribution with a high spread of atoms on the substrate, and this may be led to disappear of defect from the surface. On other hand, this may be due to the number of deposited atoms increases and thus increases of coulomb repulsion force. Figure (2c and d) showed the image of GaN with 3and 7 thin layers on PSi substrate, the irregular formation of the porous layer through the electrochemical etching process was observed. There are many smaller pits that can appear in 3 layers more than 7 layers, and there is a significant change in the distribution and volume of pores, crystals with a random orientation were of different shapes and sizes.





c d

FIGURE 2. FESEM image of GaN thin films (a) GaN/Si 3 L, (b), GaN/Si 7 L, (c)GaN/PS 3L, (d) GaN/PS 7L.

AFM

Figure3(a,b) depicts the 3-D topographic image of GaN deposited on Si with 3 and 7 layers by spin coated technique at 300 rpm with annealing at 950°C aid with NH3. The figure exhibited smooth and uniform grains and good coheres with each other, and the figure on the right shows a Gaussian distribution. When increased thickness by increase number of layers to 7layers, we notice increase in grain size and roughness, as shown in Table2. The high degree of roughness of the surface indicate it can using this layers in many applications, because of changes occurs in the optical, transitions and mechanical properties, on other hand the good degree of roughness of the surface means the possibility of using this layer as a good absorber material [24]. Figure3(c and d) describes topographic (3D) images of the GaN/PSi sample. The figures show all films have granular structure, and tendency to coalescing smaller grains into bigger, from the graphic of the diameter values distribution chart, the distribution similar to lognormal distribution. The surface roughness and R.M.S of the films decrease as a function of number of layer increase, where the roughness, R.M.S and surface thickness are associated with a direct relationship. The results revealed that the thin films GaN/PSi deposited with 3layer is more roughness and less grain size, and this is important in using it as a gas sensor, where the sensitivity can improving depending on grain size and roughness[25].

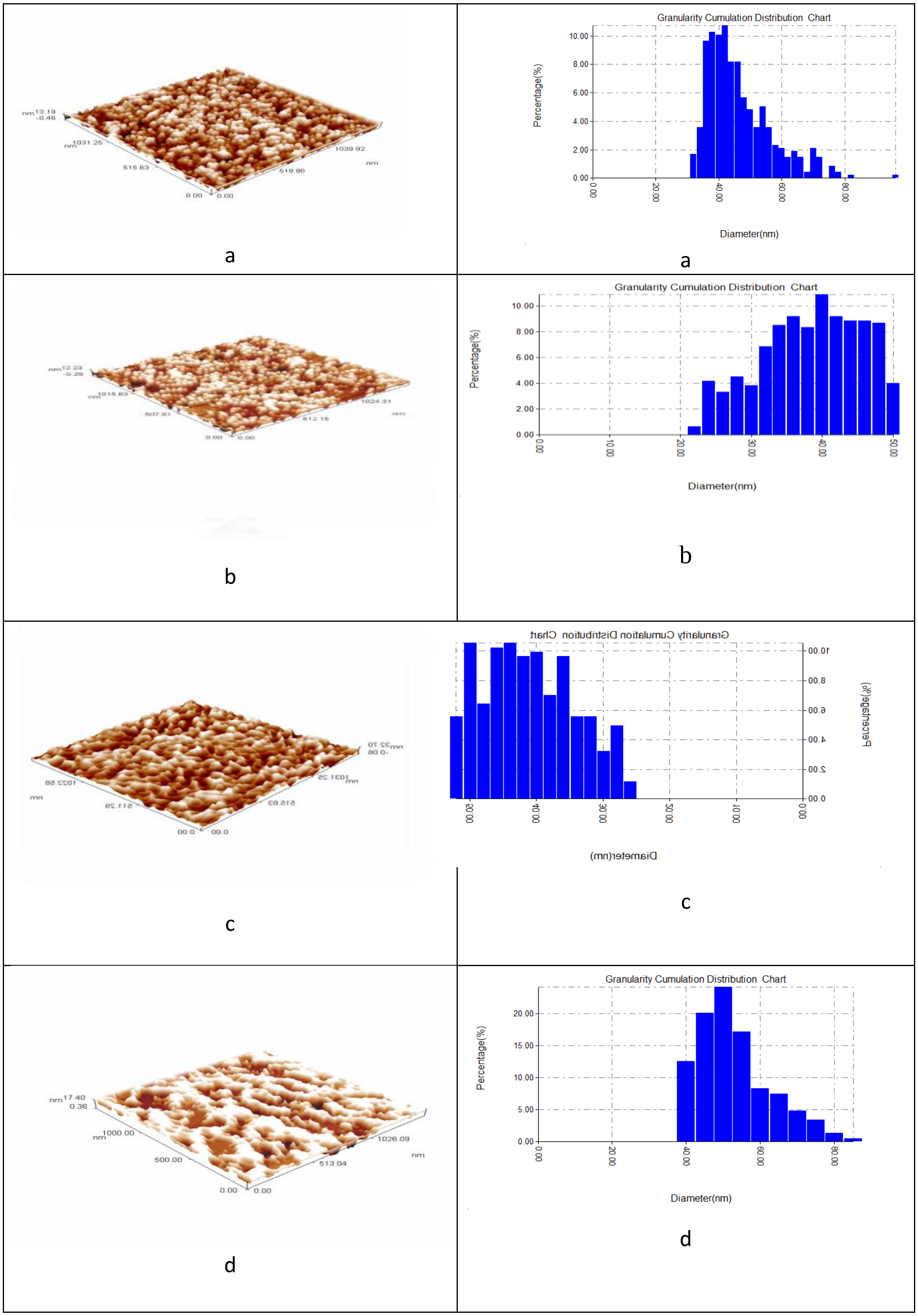


Figure 3. The atomic force microscope 2-D and 3-D Image of prepared films.

TABLE 2. Roughness, grain size, and root main square of GaN deposition on Si and PSi (3and 7L).

sample	substrate	Roughness (nm)	Grain size (nm)	R.M.S (nm)
3L	Si	1.84	66.39	2.2
7L	Si	4.41	72.97	5.17
3L	PS	7.21	37.4	8.5
7L	PS	3.4	40	3.61

Gas sensor

Figure 4 shows difference of resistance as a function of time for GaN (3 and 7 layer) on Si and PSi substrate with on/off gas valve open to 450-ppm concentration of NH3 gas at 50, 75, and 100 °C. When the surface exposed to NH3 gas, the gas will interaction with surface and will disintegrate, the hydrogen reacts with the chemically absorbed oxygen on the surface, and the hydrogen sensitivity affected when a polarized layer created near the metal (Ag)/GaN and defects on the surface [26]. Figure 4-a shows the results of the GaN/Si (3 layer), the sensitivity is about 45% as Table 3. The sensitivity enhancement significantly with increase the thickness as shown in Fig 4-b, these may be due toincrease roughness as well as AFM. The results indicated increase in sensitivity with increasing temperature operators, this is a natural result due to the conductivity of semiconductor increases with high temperatures [27]. Figure 4(c,d) showed the variation of resistance as a function of time with on/off gas valve of Ag/GaN/PSi at 3 and 7 layers. Good sensitivity about 931% at 100C comparing with GaN/Si at 3 layers. The large area of the surface of PSi plays an important role in decreasing resistance, alsothe high sensitivity may be due to the difference ratio of porosity, large surface roughness.Reduced particle size can significantly affect sensitivity improvement, where the PSi has smaller grain size than Si, i.e., it has more grain boundaries when the grain size is small, that is means the charge density are increase, because of increase interaction between NH3 gas and the grain boundaries, and therefore the sensitivity increase with decrease resistance ,these indicate the grain size proportionate inverse with sensitivity. Figures 5 (a-b) show, the diversity of NH3 gas sensitivity versus operating temperature for GaN/Si, PSi gas sensor samples as a function of number of layersrespectively. These figures show the increase in sensitivity with increasing operating temperature to reach the highest value at 100◦C,this can be attributed to the fact when the increase the temperature of substrate the atoms will obtained high energy enough to overcome the activation energy barrier, and increase in the concentration of electrons because increase the interaction between the gas and the surface and these lead to an increase in absorption and the interaction chemical, and reaction energy sufficient to complete the chemical reaction [28].

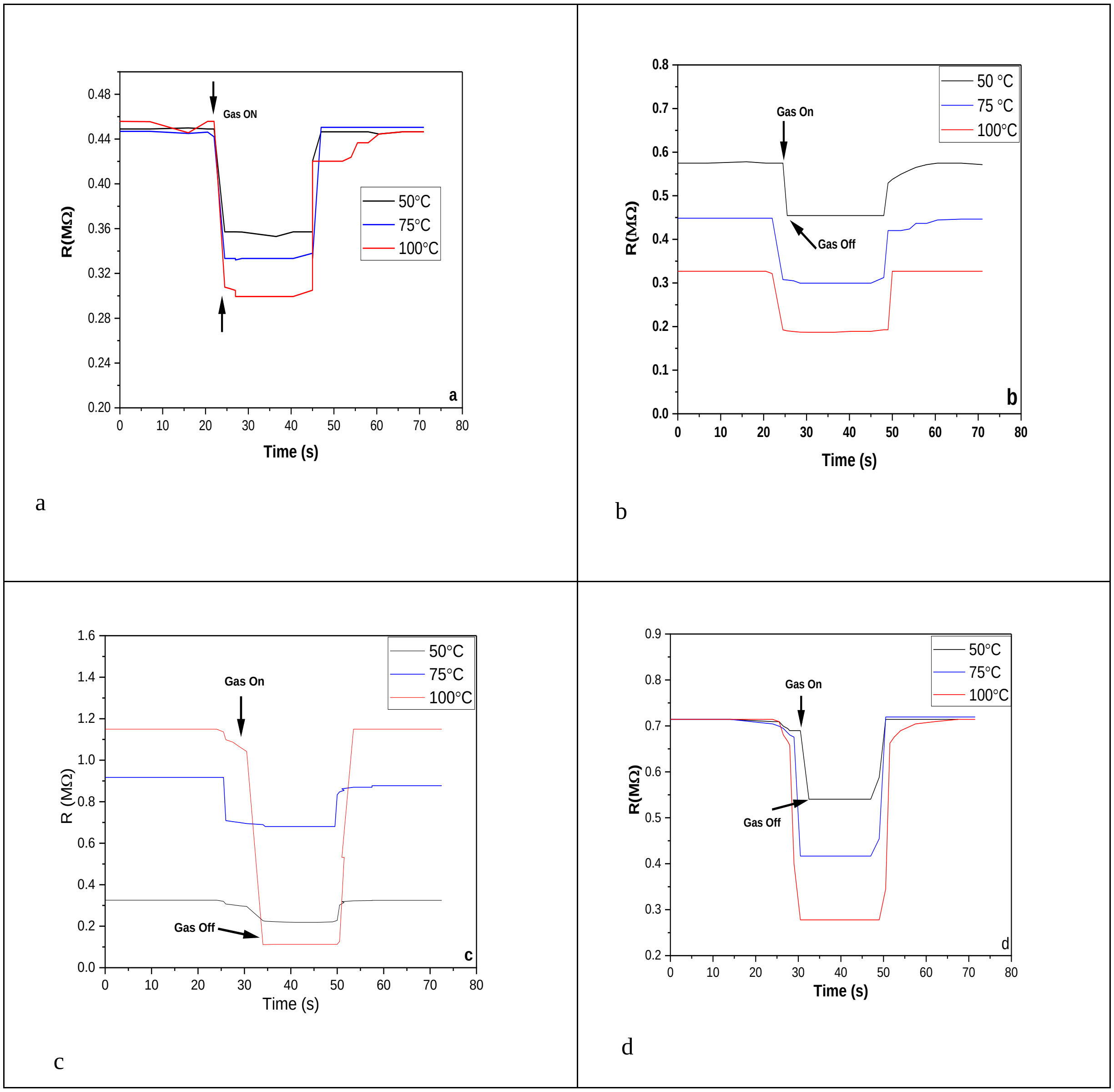


FIGURE 4. Resistance of (a)-Ag/GaN/Si(3L), (b) Ag/GaN/Si(7L), (c) Ag/GaN/PSi(3L), (d) Ag/ GaN/PSi(7L) as a function of time for NH_3 gas.

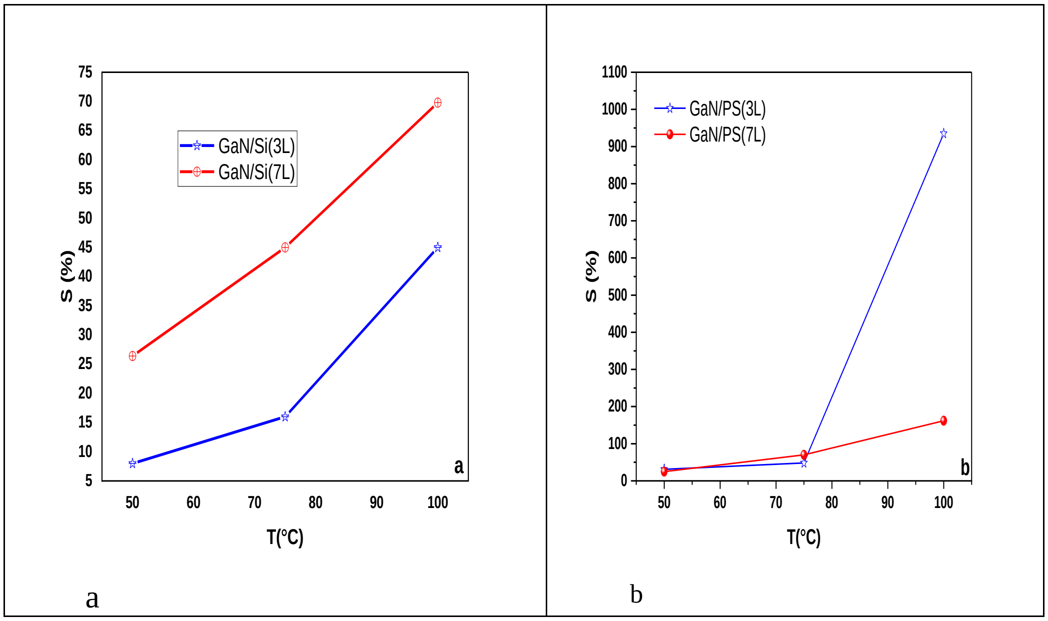


FIGURE5. Sensitivity versos temperature for (a)GaN/Si, (b) GaN/PSi as a function for number of layer.

TABLE3. Sensitivity, response and recovery time of GaN deposition on Si and PS (3and 7L).

sample	substrate	Temperature (°C)	Sensitivity (%)	Response Time (s)	Recovery Time (s)
3L	Si	50	8	12	13.5
		75	16	13.4	14
		100	45	11.8	12.4
7L	Si	50	26.4	10.8	13.3
		75	45	14	11.25
		100	69.8	10.8	12.15
3L	PS	50	31	15	9.9
		75	48.3	13.95	7.2
		100	935	15.3	13.5
7L	PS	50	25	13.5	14.4
		75	70	8.1	8.1
		100	162	9	11.25

CONCLUSIONS

The effects of number of layers on the performance of fabricated Ag/GaN/Si, and Ag/GaN/PS device examined. XRD pattern showed that GaN films crystallized in Hexagonal symmetry, exception one peak cubic phase structure. The morphological results via FESEM and AFM demonstrate uniform grains and good coheres and more roughness when deposited on porous substrate and good adherence for gas sensor. The effect of reduced of particle size on sensitivity is achieved. GaN/ PS showed high sensitivity which about 931% at 100∘C comparing with other layers. These results indicate that GaN/PS is a good candidate for toxity gas detection.

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