Development of Nitride-Sensors for Monitoring in Control Systems

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Abstract: Sensors became integrated through the control condition arrangement, either for visual, mechanical, biological, or chemical applications. New stuff is designed for detection, as Diluted Magnetic Semiconductors (DMS), and are considered attractive candidates that consist of a traditional 111- V, II-VI, or group IV semiconductor. Manganese Mn-doped GaN (Mn.Gac.N) epitaxial velum has a unique magnetic, visual and chemical properties in order to control system intelligent for detector design. The subject area of the magnetic properties of MnxGal-xN is on a large scale available, there are only a few studies on the visual properties and electrochemical properties of MnxGal-xN epitaxial velums. Where MnGaN velums were used in spintronic and opto-electronic applications according to their magnetic characterization and constructed MnGaN electrode are drop fabric potential for potentiometric sensor applications since they have good performance as ion-selective electrodes. The electrical and magnetic properties that allow the control of electron spin as well as complaint period, makes the materials ideal for spintronic applications. Designing such spintronic and optoelectronic devices based on MnxGal-xN requires a broader agreement of physical, visual, electrical and chemical properties epitaxial velums that are still seldom in the literature. This bailiwick displays the potential use of MnGaN semiconductor as an all solid-state potentiometric sensor for measuring anions in solutions in the control engineering field.

Keywords: Diluted magnetic semiconductors (DMS), Manganese Mn-doped GaN (Mn.Gac.N), Spintronic, Opto-electronic devices.

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1. INTRODUCTION

Metal-Organic Chemical Vapour Deposition (MOCVD) epitaxial film MnGaN has been examined by Secondary Electron Emission, Ultraviolet (UV) measurements, X-Ray Diffraction (XRD), Open Circuit Potential (OCP), and Energy Dispersive X-ray Spectrometer (EDS), for its crystalline quality and surface structure, optical characterization, and electrochemical properties (1).

The perfect crystal structure, magnetic properties, and distribution of elements are clearly discussed and demonstrated by high-resolution XRD and EDS measurements, which also provide the practical data for the relative calculation. Moreover, optical characterizations, for example, the energy band gap of MnGaN changes in the range 1.geV-3.5eV, are revealed by the UV measurements (2). It is a great discovery for semiconductor nanotechnology of a traditional III - V, II-VI, or group IV semiconductor (3).

The electrochemical properties of MnxGal_xN thin films are for the first time presented by Ion Selective Electrodes (ISE) (5). This study demonstrates the potential utilization of MnGaN semiconductor as an all solid-state potentiometric device for measurement of anions in solutions in the control engineering field.

The semiconductor is one of solid materials that has electrical conductivity in the middle of a conductor and an insulator. Semiconductor devices over a large scale range either permanently or dynamically (6). Semiconductor units are tremendously important in engineering science. Examples range from computers to cellular earpiece to digital audio role player. Semiconductor devices are primary in modem electrical senses of device (7, 8). The mix of various semiconductor types together creates gadgets with a special electrical property, which allows restraint of electrical signals. Silicon is used to create most commercial semiconductor units, but loads of other materials are used as well (9).

The Diluted magnetic semiconductors (DMS) considered as an important candidate for the next generation of electronic devices which consist of a traditional Trine - V, II-VI, or group IV semiconductors (6). Among of this DMS materials, manganese Mn-doped GaN (MnxGal_xN) epitaxial films gain growing interests. It is one of the ideal semiconductor materials which are under intense investigation of the diluted magnetic semiconductors (DMS) inquiry (10). It allows to interplay among electronic and magnetic properties and is structurally compatible with most epitaxial full-grown III-V semiconductors (3, 4). Thus, nanostructures of GaN-based DMS have gained attention from the expectation of new magnetic and magneto -visual properties due to the combining of the quantum parturiency and the magnetic properties peculiar to this material.

Several years ago, the field of electronics twirl (Spintronics) aimed to use spin of carriers for electronic gimmick, which has emerged as the new frontier in device physics for the future integrated technology. The thought of utilizing the spin of carrier's spintronic devices has led to efforts in fabricating and investigating appropriate new semiconductor materials (11). To make MN xGal-xN a potentially ideal material for spin-injection applications such as spin p-n diodes, spin transistor, spin detectors, spin Light Emitting Diodes (LEDs), more suggested application include: emiconductor-based spin valves, spin field effect transistors, and even spin qubits to be used as the basic building block for quantum computing which utilize both information processing and data storage within one material system (12). A combination of conventional semiconductor with magnetic materials would be very desirable. The research of analyzing the Mn storey transition free energy by optical measurements in the ultraviolet-visible region reported the strongly localized twist (S=5/2) of the Mn 3cf electrons can couple with free carriers, resulting in an effective Mn-Mn ferromagnetic interaction and a duty period in the position of Fermi level with different Mn immersion (13). According on the Linear Combination of Atomic Orbitals (LCAO) negatron band social structure of this semiconductor, the sum electron spin of the Mn corpuscle relies on the position of the Femtometer level and inter-band transition which are reported in (14).

Magnetic dimension of MnGaN films are important for the optimization of the growing conditions of magnetic devices (15). The property techniques used to measure the magnetic properties are the vibrating sample Magneto meter (VSM) and Superconducting Quantum Interference Device (SQUID). The VSM is versatile and can be used for electrical room temperature and visual control of ferromagnetism (FM) in the control organization. It needs an 'Einstein ' to manipulate data and produce a result (12). The fast speed and huge database define high requirement of hardware of the computing system. Magnetism is already exploited in recording devices such as computer hard disks. And that Information is recorded and stored as tiny magnetized sphere of smoothing iron (15). To access the knowledge, a browse mind detects the minute changes within the magnetic field because the disk twists underneath it. As this evoked corresponding changes within the head's electrical resistance-an effect known as the magnetoresistance. Read heads incorporating Giant Magneto

Resistance (GMR) stuff would be ready to sense a lot smaller magnetic line of business, allowing the storage capacity of a hard disk to extend from one to twenty GB (16). GMR sensors have a wide range of applications : they have fast accurate position and move sensing of mechanical components in precision engineering and in robotics and in robotics; all kinds of automotive sensors for fuel handling systems, antiskid systems, navigation, speed control and electronic engine control; missile guidance in the current industry; position and motion sensing in computer telecasting games as well as Key -hole surgical process and post-intelligence agent care applications.

2. Methodology

To examine the performance of constructed MnxGal-xN electrodes via the different electron and chemical field. The testing of sensitivity of inorganic and organic compound around the range of electrolyte solutions (KF, KNO_3, KCI, HOC_6H_4COONa, KSCN, CH_3COOK, $KClO_4$, KI, and KBr) with concentrations of up 1x10-^{1}M, up $1x10^{-2}$M, up $1x10^{-3}$M, up $1x10^{-4}$M, up $1x10^{-5}$M, and up $1x10^{-6}$M).

2.1 Electrochemical Measurements (Solutions)

All electrolyte solutions are prepared by reagent-grade salts (KF, KNO_3, KCI, HOC_6H_4COONa, KSCN, CH_3COOK, $KClO_4$, KBr, and KI) with nanopure water (NPW, 18.2 MΩ, Barnstead D1l9 11 Nanopure Diamond) in the laboratory. The procedure is using percentage by weight (w/v).
The formula is: [Mass of solute (g) / Volume of solution (mol)] x 100
The highest initial concentration of solutions are made in mol/ l (M); then diluted to 10^{-2} -10^{-6} M for low constructions to complete calibration curves for each type of electrodes.

2.2 Electrochemical Cell Assembly

The three-electrode electrochemical cell consisting of a reference electrode, a working electrode (semiconductor), and a counter electrode (also called an auxiliary electrode) is used for electrochemical experiments. The potential measurements are done versus a saturated calomel electrode (SCE) connected to the electrolyte by means of a salt bridge made of a glass capillary tube filled with a saturated KCI solution. The standard potential of the SCE reference electrode is EO (SCE) = 0.242V versus the normal hydrogen electrode (NHE).

A platinum wire electrode is used as the counter electrode. This electrode has a sufficiently large surface (more than 10 times larger than the surface of the working electrode) to ensure that its interface with the electrolyte does not influence the current-potential curves. To remove dissolved oxygen from the solution and to keep the cell oxygen-free throughout the experiments, the electrolytes are purged with argon gas before the measurements, and argon is blown over the solutions throughout the measurements. Before each series of measurements with a new electrolyte, the following procedures are carried out to ensure cleanliness of the equipment: 1) the platinum counter electrode is thermally treated with a gas burner to remove species that could have been adsorbed on the electrode surface from the previous electrolyte, 2) the electrochemical cell is cleaned by submerging it into a hot bath (90·C) of concentrated hydrochloric and sulphuric acids for one hour and 3) the cell is rinsed with double distilled water and NPW in that sequence. All experiments are carried out at room temperature, which is almost constant at 21±1 °C (16).

2.3 Open Circuit Potential Measurements

The open circuit potential is the potential at which there is no current; that is, experiments based on the measurement of the electrical potential of an electrode against a reference electrode of the open circuit potential. It is a potentiometric experiment.

The measurements use 12542A Frequency Response Analyzer which provides a measurement of gain and phase and two points in a system. Electrochemical interface provides simultaneous voltage and current measurements.

The salt solutions (KF, KNO_3, KCI, HOC_6f_4COONa, KSCN, CH_3COOK, $KCIO_4$,
KI, and KBr) are prepared with deionized double distilled water to produce concentrations between (10^{-1} -10^{-6} M). Electroanalytical chemical investigations are performed in a very typical three-electrode cell that included platinum counter electrode, a working electrode ($Mn_{0.1}Ga_{0.9}$ N or $Mn_{0.16}$ $Ga_{0.84}N$) and a saturated calomel reference electrode. The potential measurements are done versus a saturated calomel electrode (SCE) connected to the electrolyte by means of a salt bridge made of a glass capillary tube filled with a saturated KCL solution. The standard potential of the SCE reference electrode is EO (SCE) = 0.242V versus the normal hydrogen electrode (NHE).
To remove dissolved oxygen from solutions and to keep the cell oxygen-free throughout the experiments, argon is blown over the solutions throughout the measurements, and therefore the electrolytes are purged with argon before the experiments.

2.4 Cyclic Voltammetry (CV)

Cyclic voltammetry is an electroanalytical method that utilizes nano/micro-electrodes an unstirred solution so that the measured current and potential are limited by analyte diffusion at the electrode surface. The CV results of MnxGal-xN semiconductor can be directly related to the stability of the electrode in the studied test solutions. They are investigated by performing a series of range tests during which the potential of the electrode is scanned to highly negative and highly positive values (with respect to the electrode's OCP in the solution). They were also analyzed to determine the reactions that contribute to the observed working electrode.

3. Results and discussion

Energy Dispersive Spectroscopy (EDS) is a chemical microanalysis technique utilized within conjunction for SEM to characterize the elemental composition of the analyzed sample. The EDS x-ray detector measures the relative abundance of emitted X-ray versus their energy, MnxGaI-xN thin films EDS in Fig. 1 and 2 results revealed the bulk structure and the distribution of the element as well as characterized the elemental composition.

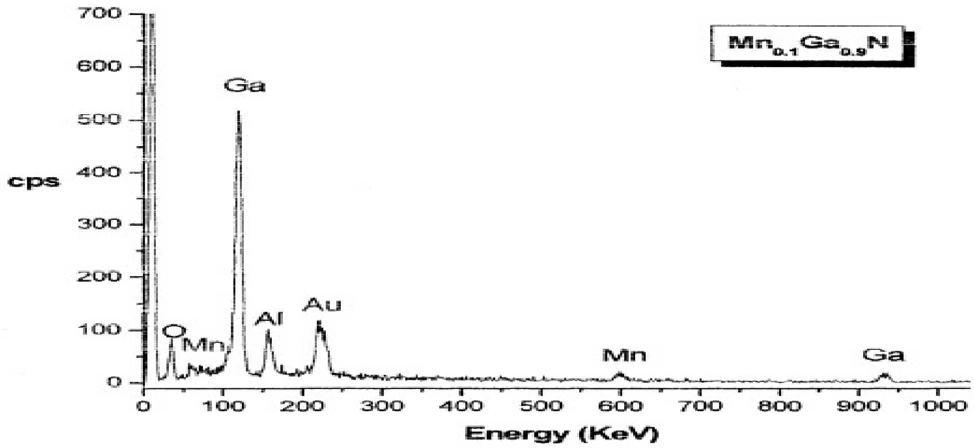

Fig. 1 The EDS results of $Mn_{0.1}Ga_{0.9}N$ thin film.

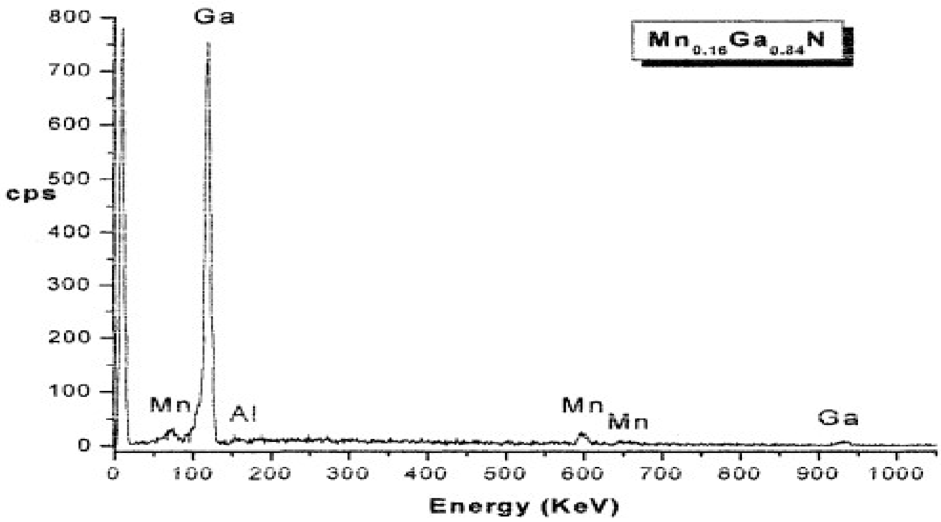

Fig. 2 EDS results of $Mn_{0.16}Ga_{0.84}N$ thin film.

The CV results of MnxGal-xN Electrodes at different salt (KF, KNO_3, KCI, KSCN, KCLO, KBr and Kl) in Table 1of the element as well as characterized the elemental composition.

Table 1 The CV Results of MnxGal-xN Electrodes

MnO.16G80.84N sample electrode, 82				MnD.lGauN sample electrode, SI				
Maximum Current		Potential		Maximum Current		Potential		Salt
Anodic	Catb1)dic	To	From	Anodic	Catbmm:	T1	From	
-	-	-	-	7	-5	-	-0.75	KF
-	-	-	-	1	-1.1	-	-0.75	KNO_3
11	-16	-03	-0.75	15	-17	-03	-0.75	KCI
4.8	-10	-0.3	-0.75	0.5	-0.85	-	-0.75	$HOC_6$1:4COO
-	-	-	-	1.25	-0.8	-	-0.75	KSCN

-	-	-	-	0.9	-0.72	-	-0.75	CH_3COOK
9	-11	-0.3	-0.75	0.76	-0.9	-	-0.75	KCLO.
13	-17	--0.3	--0.75	U	-0.85	-	-0.75	KBr
15	-15	-0.3	-0.75	1.2	-0.85	-	-0.75	Kl

3.1 Potentiometric Response

This section discusses the results obtained with the comparisons between the $Mn_{0.1}Ga_{0.9}N$ and $Mn_{0.16}Ga_{0.84}N$ electrodes. These two electrodes are made with the same semiconductor material with different concentration of Mn incorporation. Table 2 contains the OCP values measured with both sample electrodes in various electrolyte solutions. The differences have a wide range in measured OCP results between the two MnxGal_xN sample electrodes in the selected electrolyte solution. This may be attributed to the heterogeneity of the MnGaN thin film across the wafer and also the series measurements are processing in the half-year period. Therefore, the performances of two electrodes are very different. The factors that influence the response of the electrodes are investigated in more detail in the following sections.

Table 2: Variation of OCPs with Solutions for MnxGal_xN Electrodes.

Relative	Absolute	Measured OCPotential (mV)			
		SCE		Con	
					Salt
between SI and	between SI and	S2	SI		
()	(mV)	(Mno.t6GaO.8	(Mnn.l	(mol	
30	94.93	-316.85	-411.78	10-	
48	148.40	-310.03	-458.43	10-	
32	118.24	-373.94	-492.18	10-	
				10-	KCI
24	101.38	-414.21	-515.59	2	
43	189.34	-445.44	-634.78	10-	
44	203.03	-459.20	-662.23	10-	
71	155.20	-218.35	-373.55	to-^{6}M	
55	140.61	-255.83	-396.44	10-	
22	66.50	-307.05	-373.55	10-	
22	83.10	-371.37	-454.47	10-	$HOC_6R.COO$
16	65.61	-410.20	-475.81	10^{-2}	
8	35.00	-431.43	-466.43	10-	
5	14.15	-314.15	-328.30	10-	
24	77.77	·321.03	-398.80	10-	
34	121.97	-359.93	-481.90	10-	
14	60.75	-436.95	-497.70	10-	$KCI0_4$
11	53.73	-472.87	-526.60	10-	
9	43.86	-494.14	-538.00	to-	

3	11.21	-375.22	-364.01	10-	
39	120.11	-309.17	-429.28	IO-	
31	114.01	-372.83	-486.84	10-	
				10-	KBr
22	92.93	-428.92	-521.85	[illegible]	
22	98.56	-458.06	-556.62	to-	
30	140.18	-469.05	-609.23	10-	
1	3.96	-392.86	-388.90	10-	
35	116.83	-333.38	-450.21	10-	
33	130.55	-399.10	-529.65	10-	
				10-	KI
21	100.25	-468.44	-568.69	[illegible]	
20	99.11	-496.08	-595.19	to-	
22	109.17	-501.00	-610.17	to-	

Epitaxial layers of MnxGal_xN with concentrations of (x=0.l or 0.16) have been grown on GaN(OOOl)/sapphire(OOOl) by metalorganic chemical vapor deposition (MOCVD). Two different samples $MO_{0.1}$ $Ga_{0.9}N$ and Mno.16Gao.84N - are analyzed by X-ray Diffraction (XRD), Secondary Electron Emission/Energy Dispersive X-ray Spectrometer (SEMlEDXS), Ultraviolet (UV) measurements, and Open Circuit Potential (OCP). All the experiments and observations are under room temperature.

Crystalline quality and surface structure of MnxGaJ_xN are measured by XRD. The results displayed no significant deterioration in crystal quality and the increasing of surface roughness with the incorporation of Mn. The single crystal structure and pattern distance are proved by the calculation.

The SEMIEDS results provide the interface pattern and the elements distribution analysis. It is found that the Mn atoms are mostly concentrated in one section of the surface.

The energy band gaps of the samples are determined by UV measurements. It is found that the energy band gap changes in the range of 1.0 eV-3.5 eV regarding the concentration of Mn. The Linear Combinations of Atomic Orbitals (LCAO) electron band structure of MnxGaJ_xN semiconductor compound alloy is determined. It is found that the total electron spin of the Mn atom depends on the position of the Fermi level and interband transitions in the electron band diagram of MnxGal_xN. The optical properties of the wurtzite MnxGal-xN are determined as well.

OCP measurements revealed the sensitivity of the samples (MnxGat-xN) on a wide range of anionic concentrations. The fabricated MnxGal_xN sample electrodes showed a good response to Cl', Br'', r, CI04- compared to all tested organic and inorganic anions. They also demonstrated good chemical and mechanical stability and hence, MnxGal_xN semiconductors could be employed to construct ion-selective electrodes that are both durable and easy to use. The study also showed that some of the electrode characteristics and specifically, their region of linearity and the reproducibility of OCP results leave space for improvement and necessitate further research, as shown in Fig 3.

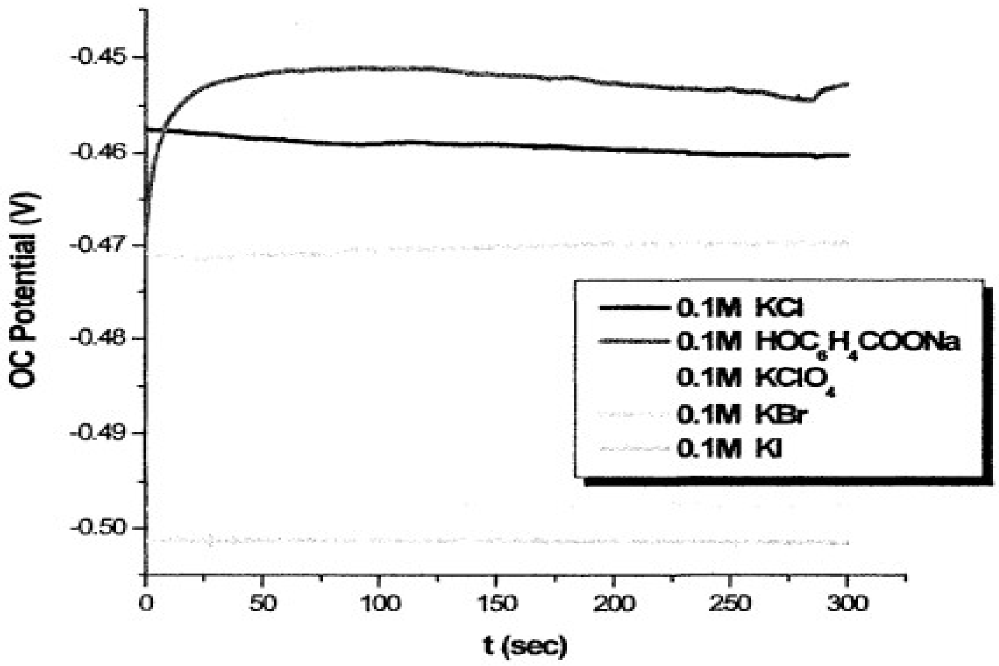

Fig. 3 The variation of OCP with time for $Mn_{0.16}Ga_{0.84}N$ electrode.

In view of the above perceptions, the MnGaN surface is often thought of as a perfect transducer for the event of composite membrane based sensors. For this, nine anion solutions (l0-IM-IO-6M) are investigated via OCPs experiments of the MnGaN electrodes, and the response to the potassium, bromine, iodine, and perchlorate anions is investigated, under the same experimental conditions as shown in Fig 4. The composite electrodes (sensor) had reproducible response and very fast to potassium activity changes. On the other hand, the slope of the sensor is very close to the theoretically expected one. MnGaN (0001) surface is shown to selectively interact with anions in solution, based on the potentiometric response of the MnGaN surface to anions with drastically different lipophilicities.

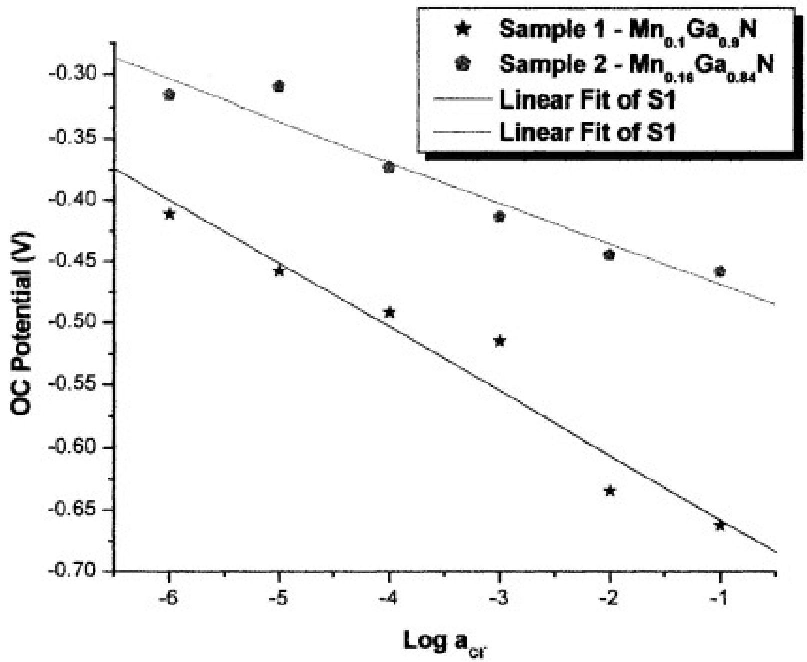

Fig. 4 Calibration curve of the $Mn_{0.1}Ga_{0.9}N$ and $Mn_{0.16}Ga_{0.84}N$ in five test electrolytes.

4. Conclusions

Chemical sensors have a wide application with the control system in the environmental and food industry. Biosensors, especially, electrochemical sensors have become increasingly important as biochemical and biological applications always emerge. These kinds of applications include: food monitoring, automotive, medical diagnostics, home/environmental monitoring, and high throughput screening (HTS), biological/chemical warfare (Homeland Security) and industrial applications. Potentiometric electrodes are the one type of electrochemical sensors which requires, for operating, a voltmeter resolution range between 1 mV to 1 Volt. Potentiometric sensors normally use linear sweep voltammetry and cyclic voltammetry to determine the redox potentials of the ion adsorbed at the sensor surface. Since MnGaN electrodes have stable cyclic voltammetry (CV) results as well as impedance, it has great potential in all solid-state potentiometric sensors application. MaGaN semiconductor material has great potential to develop the GMR sensor and potentiometric sensors of control systems.

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