

Sulfide and Fluoride Ions Based Passivation of GaAs(100) Surface

Pawan Tyagi^{1,2*},

¹ Department of Mechanical Engineering, University of the District of Columbia, Washington DC-20008

²Department of Materials and Metallurgical Engineering, Indian Institute of Technology Kanpur, UP-208016, India

ABSTRACT

Sulfur interaction with GaAs can reduce the harmful effect of surface states on recombination attributes. Apart from surface passivation, study of sulfur bonding on GaAs is also important for developing novel molecular electronics and molecular spintronics devices, where a molecular channel can be connected to at least one GaAs surface via thiol functional group. However, the primary challenge lies in increasing the stability and effectiveness of the sulfur passivated GaAs. We have investigated the effect of single and double step surface passivation of n-GaAs(100) by using the sulfide and fluoride ions. Our single-step passivation involved the use of sulfide and fluoride ions individually. However, the two kinds of double-step passivations were performed by treating the n-GaAs surface. In the first approach GaAs surface was firstly treated with sulfide ions and secondly with fluoride ions, respectively. In the second double step approach GaAs surface was first treated with fluoride ions followed by sulfide ions, respectively. Sulfidation was conducted using the nonaqueous solution of sodium sulfide salt. Whereas the passivation steps with fluoride ion was performed with the aqueous solution of ammonium fluoride. Both sulfidation and fluoridation steps were performed either by dipping the GaAs sample in the desired ionic solution or electrochemically. Photoluminescence was conducted to characterize the relative changes in surface recombination velocity due to the single and double step surface passivation. Photoluminescence study showed that the double-step chemical treatment where GaAs was first treated with fluoride ions followed by the sulfide ions yielded the highest improvement. The time vs. photoluminescence study showed that this double-step passivation exhibited lower degradation rate as compared to widely discussed sulfide ion passivated GaAs surface. We also conducted surface elemental analysis using Rutherford Back Scattering to decipher the near surface chemical changes due to the four passivation methodologies we adopted. The double-step passivations affected the shallower region near GaAs surface as compared to the single step passivations.

INTRODUCTION

GaAs is one of the most important electronic materials for the fabrication of lasers [1], quantum dot [2], high-speed devices for the optical and mobile communication[1]. GaAs is also promising for molecular electronic devices [3]. Molecules can be utilized as a device element or passivants [4]. However, utilization of the full potential of GaAs is a challenging task and depend on how effectively surface passivation is accomplished [5]. A GaAs surface possesses myriad of density of surface states at oxide/GaAs interface. An interface of GaAs and imperfect oxide possess unsaturated dangling bonds associated with GaAs surface atoms and various surface defects [6]. These dangling bonds severely increase the surface recombination velocity, increase charge depletion region near the surface, and pinned the surface Fermi level near mid-

band gap. A number of attempts were made to deactivate the high density of surface states using several elements and compounds for more than two decades, but without any discovery of the permanent solution [5, 7]. The sulfur (S) passivation has been one of the most successful surface treatments yielding significant improvement in surface electrical properties. This S passivation approach drew the considerable attention of researchers [7, 8]. Furthermore, electrochemical charging of sulfur yielded higher and more stable improvement in surface electrical properties [9]. Recently, improved S passivation involving highly controlled atmosphere and high temperature annealing yielded ideal surface electrical properties[10, 11]. However, such intricate surface passivation methodologies involving high-temperature and ultra-high vacuum make a fabrication process uneconomical and also affect the efficacy of other production steps. There is a critical need of finding a fast and near room temperature GaAs surface passivation. Under this quest we have attempted single and double step GaAs surface passivation by utilizing sulfide and fluoride ions. We choose fluoride ion in conjunction with sulfur due to its potential role in decreasing surface states in the prior study [12]. In this paper we report our passivation methodologies and the study about their impact on GaAs surface states and composition.

EXPERIMENTAL METHOD

All surface passivation schemes were attempted on n-GaAs(100) samples with $3 \times 10^{18} \text{ cm}^{-3}$ dopant concentration. Every wafer piece was degreased by sequentially dipping in trichloromethane, acetone, and methyl alcohol for 1 min each. Just before passivation treatment GaAs surface was deoxidized with HCl:H₂O (1:4) solution for 2 min, followed by rinsing in DI water for 1 min and finally drying in nitrogen flow. A sulfide ion solution, with 140 mg/liter sulfide ion concentration, was prepared by dissolving Na₂S in t-butanol. However, 220 gram/liter fluoride solution was produced by dissolving NH₄F in deionized water. Previous studies showed that sulfide ion based passivation produced best results with Na₂S salt dissolved in low dielectric organic solvent, especially t-butanol ($\epsilon=12.47$) [11]. However, we did not choose organic solvent for NH₄F salt. This salt exhibited very poor solubility in organic solvent yielding 0.2 mg/liter fluoride ion concentration. Hence, aqueous fluoride ion solution was utilized for four passivation schemes. Two passivation schemes involved single step passivation with sulfide and fluoride ion alone. Whereas, two double steps passivations utilized both fluoride and sulfide ions. The single step sulfidation (fluoridation) were performed simply by dipping GaAs samples in sulfide (fluoride) ion solution for 10 min and passivated sample were named as S(F). A double step passivation scheme was

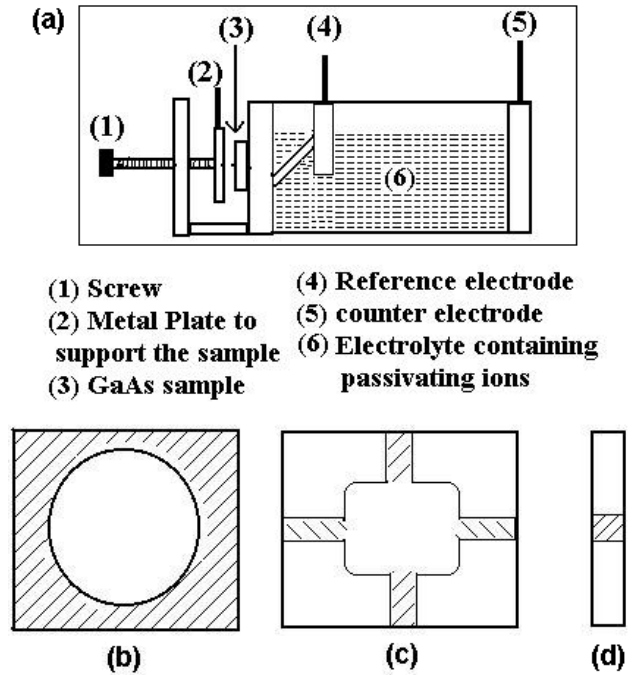


Figure 1: (a) Electrochemical experimental setup for electropassivation. Hatched area shows metalized section on (b) front, (c) back, and (d) side edges of a GaAs rectangular sample prepared for electrochemical passivation in (a).

executed by first dipping the sample in fluoride (sulfide) solution and then in sulfide (fluoride) solution for 10 min in each solution, and sample were named as FS(SF). In between two steps for the double step passivation a water rinse was performed. Delay between the two steps was less than 2 min.

To study the effect of passivant charging method, sulfide and fluoride ions were also charged electrochemically on GaAs surface. This step was performed in a customized electrochemical cell and GaAs metallized with indium metal (Figure 1). The experimental set up, as shown in Fig.1a, was utilized to electrochemically passivate the metallized sample (Figure 1(b-d)). Indium metal was used to metallized the GaAs sample on the front (Figure 1b), back (Figure 1c), and at the edges (Figure 1d). During electrochemical charging $1\mu\text{A}/\text{cm}^2$ anodic current was applied on GaAs surface for 10 min. Current was controlled with potentiostat (Model 263A EG&G Princeton Applied Research). During electrochemistry, sulfide/fluoride solutions were utilized as electrolyte, silver/silver chloride was utilized as a reference electrode, and platinum mesh was utilized as counter electrode. Within 10 minutes after passivation treatment(s) samples were rinsed and dried in nitrogen flow, and were studied by the photoluminescence study. Efficacy of various passivation schemes was evaluated by measuring the photoluminescence intensity (PLI). For the PLI study, a Spectra-Physics 165 Ar ion laser was fixed to operate at 150 mW at the source end with 530.15 nm light excitation wavelength. To gauge the change in surface chemistry of passivated samples RBS study was performed. For this study, a 2 MeV Van de Graaf accelerator, with detector aligned at 30° from the line of an incident of helium ions, was used. Bombarding helium ion beam induced a 5-10 nA charge on a sample surface.

RESULTS AND DISCUSSION

Measurement of PLI is directly associated with measurement of surface recombination velocity, which in turn depends on the density of surface states due to dangling bonds and near surface defects. The high density of surface states reduces the PLI by decreasing radiative recombination of laser excited electron-hole pairs. The magnitude of average PLI on FS (sample treated with fluoride ion and by the sulfide ions) was slightly higher than the PLI seen on S sample. The PLI for FS and S samples were 2729 ± 20 and 2560 ± 80 , respectively (Figure 1). It appears that the first fluoridation step conditioned the GaAs surface to improve the sulfidation impact. As a result, FS showed lower recombination than that of S alone. Interestingly, S and FS both exhibited distinctively higher PLI than that observed on F and SF samples. The PLI for F and SF were 1800 ± 30 and 2010 ± 30 , respectively (Figure 1). We hypothesized that fluoride ion is more aggressive than sulfide ion. Due to the aggressive chemical activity fluoride ion might undo the impact of sulfide ions and establish chemical bonds.

It is noteworthy that sulfidation was effective in reducing surface oxide and promoting Ga-S bonds to quench the surface states [13]. The bonding and antibonding levels for Ga-S

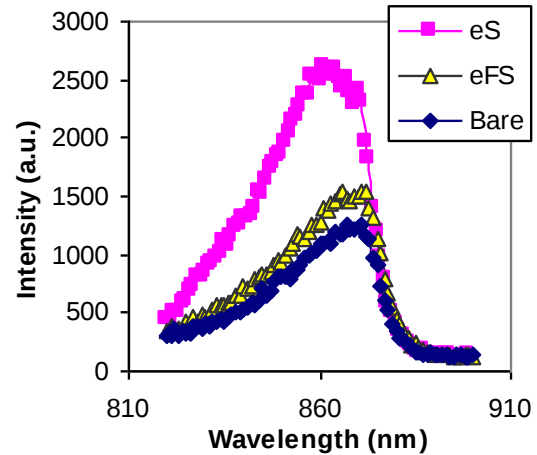


Figure 2: PLI study of electrochemically passivated GaAs.

bonds lied outside the GaAs energy band gap [10, 14]. Fluoridation is expected to produce rather stable Ga-F bonds to passivate the surface states. On the other hand, fluoride ions yield volatile As-F bonds [15], which are unable to provide stable passivation effect. According to FTIR study a fluoride ion treated surface loose most of the fluoride ions after annealing at 300 °C. However, sulfide ion treated GaAs were stable for higher temperature.

Furthermore, S and FS passivation schemes were selected for the further improvement. For the improvement, sulfide and fluoride ion charging method was switched from dipping method to electrochemical ion charging method. The method of electrochemical ion charging is provided in the experimental section. The electrochemical sulfidation step is named as eS. The eS method showed ~10% increase in PLI

(Figure 2) as compared to the PLI on S sample where sulfidation was conducted by the dipping method (Figure 1). Also, the peak of the photoluminescence data shifted by 6 nm as compared to the peak of photoluminescence data for the S sample.

According to prior studies, the electrochemical sulfidation promotes high oxidation states compounds like Ga_2S_5 and As_2S_5 on the surface [9, 16]. These high oxidation state sulfides provide more stable surface passivation than the dipping type sulfidation method [9, 16]. Surprisingly, in our study eFS samples showed low PLI increase (Figure 2) as compared to PLI observed on SF samples (Figure 2). In fact, eFS's PLI was very close to the untreated bare GaAs sample (Figure 2). We do not have the clear understanding of the exact mechanism. However, we presume that this phenomenon is due to the blocking of GaAs surface by the fluoride ions that precluded the formation of high oxidation state Ga and As sulfides during electrochemical sulfidation. In future, attempts can be made to improve such multi-ion passivation by maneuvering the solution chemistry and process duration. However, we concluded that dipping based passivation is better for FS method.

We also tested the stability of multi-ion passivation approach. All the four dipping based passivation schemes, F, S, FS, and SF were tested for the stability under laser irradiation for 10 min each in the ambient condition. The slope of intensity vs. time graph for each sample was obtained by a linear fit and was termed as degradation coefficient (Figure 3). Degradation coefficient was highest in magnitude for S sample, -0.3577. FS sample exhibited -0.1533 degradation coefficient. This data indicated that FS is more stable than the S samples. Interestingly, F and SF samples showed unnoticeable degradation over a 10-minute test duration. It appears that fluoride ion passivated surfaces are stable against light radiation. We also observed that bare deoxidized samples showed an increase in PLI during light exposure. It is presumably due to a small degree of passivation due to the radiation activated surface oxidation. GaAs oxides have been reported to provide a small degree of surface passivation[17].

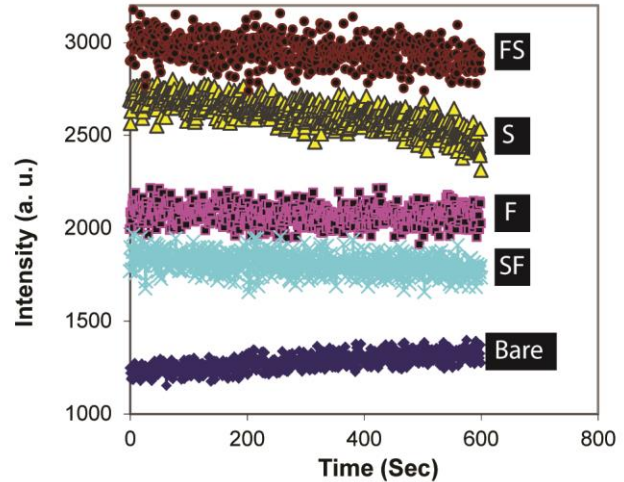


Figure 3: Photoluminescence vs. time graph for different passivation methods.

We also investigated the range of depth influenced by the various passivation methods. RBS study was utilized to evaluate the change in the surface composition of differently passivated GaAs samples. For the qualitative understanding of the change in the stoichiometry of near surface GaAs, we measured the slope of RBS spectra near the surface. The near surface RBS spectra were recorded in 375-390 channel number range (Figure 4). The slope of near surface RBS data was attributed to the composition gradient. Then each gradient was divided by the gradient observed for the bare GaAs sample (Table 1). According to RBS data, bare unoxidized sample before any passivation treatment showed a gradient of -115 magnitudes. However, passivated samples exhibited a change in composition gradient, from -115 to -37.6. High slope for S treatment (ratio 0.33 in Table 1) showed that sulfidation impact was deepest among all the passivation approach. It is apparent that the impact of sulfide ion produced most pronounced impact on GaAs stoichiometry near surface. On the other hand single step F impacted lowest depth range of GaAs surface (ratio 0.92, Table 1). It appears that fluoride ion formed compounds with Ga and As in a subsurface region. Net sublayer thickness will be governed by the diffusion of ions and etching of GaAs during passivation. We are unable to quantify exact depth based on RBS data. SF and FS samples showed 0.53 and 0.5 composition gradient ratio, respectively (Table 1). We surmise that fluoride ions cause an etching that competes with sulfide ion penetration capacity. Comparison between S and FS suggest that is more promising for field effect type device fabrication. It is noteworthy that the passivant's deeper diffusion can adversely impact the GaAs high mobility and other characteristics throughout the region where passivant is present. Hence it is utmost important to confine the passivant impact on surface chemistry in proximity of surface. The PLI measurement also favored FS treatment.

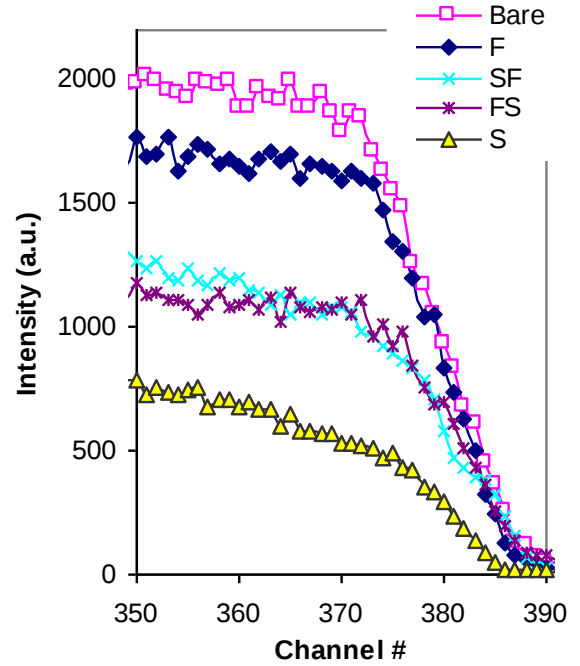


Figure 4: RBS spectra of GaAs samples treated with four passivation methods.

Table 1: Slope of RBS data for GaAs samples passivated by different methods. The third column is the ratio slope for passivated samples and bare sample.

Sample	Composition Gradient(RBS)	Composition gradient Ratio(Passivated/bare GaAs)
Bare	-115	1
F	-106	0.92
S	-37.6	0.33
SF	-61.19	0.53
FS	-57.508	0.50

CONCLUSIONS

Fluoride and sulfide ions were used alone and also in conjunction with each other to passivate the n-GaAs surface. Double step passivation involving fluoridation followed by sulfidation appears to be the best among four approaches. This scheme resulted in comparable improvement in surface recombination velocity as compared to single step sulfidation. However, advantageously FS produced more stable passivation and thinner sublayer on GaAs surface as compared to single step sulfidation approach for passivation. We also noted the FS was much better than SF passivation treatment. We surmise that fluoride ions are highly reactive towards GaAs and damaged the sulfur passivation coating to establish own chemical bonds. However, for FS, fluoride ions appear to favorably condition the GaAs for enhancing the following sulfidation treatment. It was found that FS approach impacted smaller depth of GaAs as compared to that observed for S approach. RBS study suggested that FS is more promising for field effect type device fabrication. It is critical to account for passivant diffusion depth since passivant presence will impact the GaAs high mobility and other characteristics. Further improvement is possible by the parameter optimization for the FS approach.

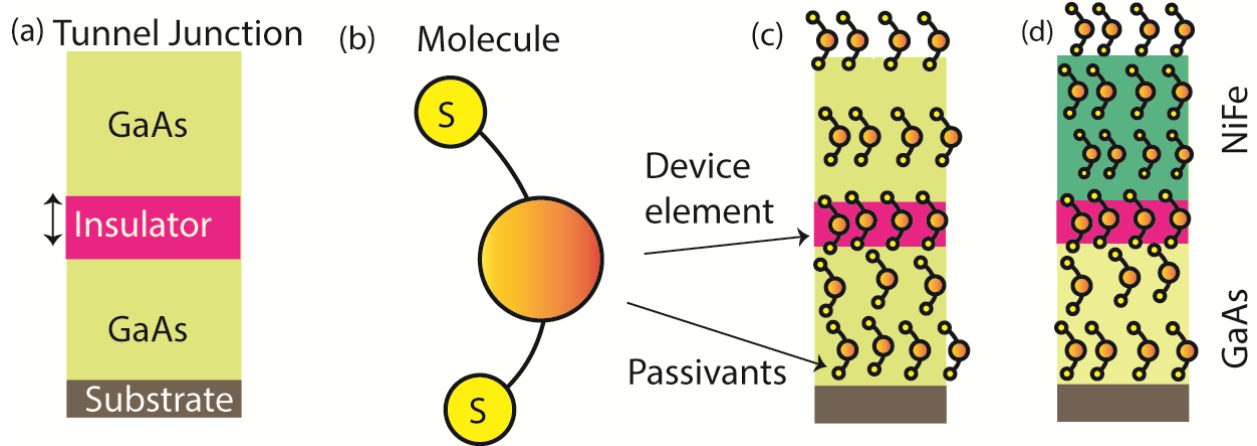


Figure 5: (a) Tunnel junction with insulator thickness < (b) length of molecule with at least two thiol (S) groups to interact with (c) GaAs as a device element and as a passivant (d) Tunnel junction with one GaAs electrode and one ferromagnetic electrode can be utilized. Ferromagnet can serve as a source of spin or spin detector.

The electrochemical sulfidation was effective in chemically bonding S with GaAs electrode. We propose that GaAs may be employed in a tunnel junction based molecular device scheme (Fig. 5) [18-26]. Under this approach a tunnel junction with the exposed edge can be produced in such a way that thickness of insulating gap (Fig. 5a) is less the length of the molecule with at least two thiol ends (Fig. 5b)[25]. It is anticipated that the molecule bridging the insulating gap will serve as the device element and will govern the transport characteristics (Fig. 5c). Whereas, excess of molecules with thiol terminal will interact with exposed GaAs surface and will serve as the passivants (Fig. 5c). One of the GaAs can be replaced with a metallic electrode, e.g., NiFe ferromagnetic electrode (Fig. 5e) to produce molecular spintronics devices. Ferromagnetic electrodes in the molecular device can serve as the source of spin or detector of spin. Also, if GaAs is doped to acquire magnetic nature than the same molecule can also serve the additional role of establishing strong exchange coupling between the GaAs and ferromagnetic electrode leading to highly correlated materials, that can be termed as molecule-based metamaterials with unique physical properties[26-28]. In our prior study[26-28], paramagnetic molecules established unprecedented strong exchange coupling between two ferromagnetic electrodes. This exchange coupling resulted in intriguing current suppression and spin-dependent photovoltaic effect.

ACKNOWLEDGMENTS

PT dedicates this paper to his former MS thesis advisor the late Prof. R. Balasubramaniam for providing invaluable skills and knowledge about technical writing and research. PT also acknowledges Dr. Deepak Kumar's for serving as the co-advisor and help with experiments. The research findings are from PT's unpublished MS thesis.

REFERENCES

- [1] S. Adachi, "GaAs, AlAs, and $\text{Al}_x\text{Ga}_{1-x}\text{As}$: Material parameters for use in research and device applications," *J. App. Phys.*, vol. 58, pp. R1-R29, 1985.
- [2] D. Gammon, E. Snow, B. Shanabrook, D. Katzer, and D. Park, "Fine structure splitting in the optical spectra of single GaAs quantum dots," *Phys. Rev. Lett.*, vol. 76, p. 3005, 1996.
- [3] R. Cohen, L. Kronik, A. Shanzer, D. Cahen, A. Liu, Y. Rosenwaks, *et al.*, "Molecular control over semiconductor surface electronic properties: Dicarboxylic acids on CdTe, CdSe, GaAs, and InP," *J. Am. Chem. Soc.*, vol. 121, pp. 10545-10553, 1999.
- [4] J. R. Heath, "Molecular electronics," *Annual Review of Materials Research*, vol. 39, pp. 1-23, 2009.
- [5] H.-H. Lu, L. Liu, J.-P. Xu, P.-T. Lai, and W.-M. Tang, "Improved Interfacial and Electrical Properties of GaAs MOS Capacitor With LaON/TiON Multilayer Composite Gate Dielectric and LaON as Interfacial Passivation Layer," *IEEE Trans. Elec. Dev.*, vol. 64, pp. 1535-1540, 2017.
- [6] N. G. Einspruch and W. R. Wisseman, *GaAs Microelectronics: VLSI Electronics Microstructure Science* vol. 11. Orlando, San Diego, New York, London, Toronto, Montreal, Sydney, Tokyo: Academic Press, 2014.
- [7] S. Jiang, G. He, S. Liang, L. Zhu, W. Li, C. Zheng, *et al.*, "Modulation of interfacial and electrical properties of HfGdO/GaAs gate stacks by ammonium sulfide passivation and rapid thermal annealing," *J. Alloy. Compd.*, vol. 704, pp. 322-328, 2017.
- [8] Y. Dong, X. Ding, X. Hou, Y. Li, and X. Li, "Sulfur passivation of GaAs metal-semiconductor field-effect transistor," *Appl. Phys. Lett.*, vol. 77, pp. 3839-3841, 2000.
- [9] X. Hou, W. Cai, Z. He, P. Hao, Z. Li, X. Ding, *et al.*, "Electrochemical sulfur passivation of GaAs," *Appl. Phys. Lett.*, vol. 60, pp. 2252-2254, 1992.
- [10] H. Hasegawa, T. Saitoh, S. Konishi, H. Ishii, and H. Ohno, "Correlation Between Photoluminescence And Surface-State Density On GaAs-Surfaces Subjected To Various Surface Treatments," *Jpn. J. Appl. Phys.* 2, vol. 27, pp. L2177-L2179, Nov 1988.
- [11] V. N. Bessolov, M. V. Lebedev, and D. R. T. Zahn, "Raman scattering study of surface barriers in GaAs passivated in alcoholic sulfide solutions," *J. Appl. Phys.*, vol. 82, pp. 2640-2642, Sep 1 1997.
- [12] K. Frese and S. R. Morrison, "Passivation and interface state studies on n-GaAs," *Appl. Surf. Sci.*, vol. 8, pp. 266-277, 1981.
- [13] B. Cowans, Z. Dardas, W. Delgass, M. Carpenter, and M. Melloch, "X-ray photoelectron spectroscopy of ammonium sulfide treated GaAs (100) surfaces," *Appl. Phys. Lett.*, vol. 54, pp. 365-367, 1989.

- [14] X. Jin, M. Mao, Y. Luo, G. Dong, P. Chen, and X. Wang, "The electronic structure of (NH₄)₂Sx treated GaAs (100) surface studied by UPS and XPS," *Vacuum*, vol. 41, pp. 1061-1062, 1990.
- [15] L. R. Williston, I. Bello, and W. M. Lau, "X-Ray Photoelectron Spectroscopic Study Of The Interactions Of Fluorine Ions With Gallium-Arsenide," *J. Vac. Sci. Tech. A*, vol. 10, pp. 1365-1370, Jul-Aug 1992.
- [16] Z. Li, X. Hou, W. Cai, W. Wang, X. Ding, and X. Wang, "A mild electrochemical sulfur passivation method for GaAs (100) surfaces," *J. Appl. Phys.*, vol. 78, pp. 2764-2766, 1995.
- [17] T. Sawada, H. Hasegawa, and H. Ohno, "Electronic-Properties Of A Photochemical Oxide-GaAs Interface," *Jpn. J. Appl. Phys.*, vol. 26, pp. L1871-L1873, Nov 1987.
- [18] P. Tyagi, "PhD Thesis: Fabrication and Characterization of Molecular Spintronics Devices," University of Kentucky (<http://archive.uky.edu/handle/10225/878>), Ph.D2008.
- [19] P. Tyagi, "Molecular Spin Devices: Current Understanding and New Territories," *Nano*, vol. 4, pp. 325-338 2009.
- [20] P. Tyagi, "Multilayer Edge Molecular Electronics Devices: A Review," *J. Mater. Chem.*, vol. 21, pp. 4733-4742, 2011.
- [21] P. Tyagi, "Molecular Electronics And Spintronics Devices Produced By The Plasma Oxidation Of Photolithographically Defined Metal Electrode " *App. Phys. A: Mat. Sci. & Proc.*, vol. 108, pp. 529-536, 2012.
- [22] P. Tyagi, "Fabrication of Tunnel Junction based Molecular Electronics and Spintronics Devices " *J. Nanoparticle Res.*, vol. 14, p. 1195, 2012.
- [23] P. Tyagi, E. Friebe, and C. Baker, "Addressing The Challenges Of Using Ferromagnetic Electrodes In The Magnetic Tunnel Junction-Based Molecular Spintronics Devices," *J. Nanoparticle Res.*, vol. 17, p. 452, Nov 2015.
- [24] P. Tyagi and T. Goulet, "Nanoscale Tantalum Layer Impacting Magnetic Properties Of Tunnel Junction-Based Molecular Devices," *MRS Comm.*, pp. 1-5, 2018.
- [25] P. Tyagi, D. F. Li, S. M. Holmes, and B. J. Hinds, "Molecular Electrodes At The Exposed Edge Of Metal/Insulator/Metal Trilayer Structures," *J. Am. Chem. Soc.*, vol. 129, pp. 4929-4938, Apr 25 2007.
- [26] P. Tyagi, C. Riso, and E. Friebe, "Magnetic Tunnel Junction Based Molecular Spintronics Devices Exhibiting Current Suppression At Room Temperature," *Organic Electronics*, vol. 64, pp. 188-194, 2019.
- [27] P. Tyagi, C. Baker, and C. D'Angelo, "Paramagnetic Molecule Induced Strong Antiferromagnetic Exchange Coupling on a Magnetic Tunnel Junction Based Molecular Spintronics Device," *Nanotechnology*, vol. 26, p. 305602, 2015.
- [28] P. Tyagi and E. Friebe, "Large Resistance Change on Magnetic Tunnel Junction based Molecular Spintronics Devices," *J. Mag. Mag. Mat.*, vol. 453, pp. 186-192, 2018.