

Shailendra Kumar Saxena, Ph.D.  
Postdoc Fellow  
National Institute for Nanotechnology,  
University of Alberta, Edmonton Canada  
✉: shailendra.saxena3@gmail.com, sksaxena@ualberta.ca  
☎: (+91) 9981366616 (India), (+1)587-937-0817 (Canada)

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## Current Research

Molecular Electronics, Device Physics, Raman Spectroscopy, Fano Scattering,  
Optoelectronic Properties of Materials, Nanoscience and Nanotechnology

## Education and Research Experience

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|---|-----------------------------|
| • <b>National Institute for Technology (NINT),<br/>University of Alberta, Edmonton, Canada</b><br>Postdoc Fellow    | <b>July 2017-Present</b>    |
| • <b>Indian Institute of Technology (IIT) Indore, India</b><br>Research Associate                                   | <b>Sept. 2016-July 2017</b> |
| • <b>Indian Institute of Technology (IIT) Indore, India</b><br>Ph.D. (Physics)                                      | <b>July 2016-Sept. 2016</b> |
| • <b>M.J.P. Rohilkhand University Bareilly U.P., India</b><br>M.Sc. (Physics)<br>specialization: <i>Electronics</i> | <b>2010</b>                 |
| • <b>M.J.P. Rohilkhand University Bareilly U.P., India</b><br>B.Sc. Physics Chemistry and Mathematics               | <b>2008</b>                 |
| • <b>Uttar Pradesh (UP) School Board</b><br>10+2  | <b>2005</b>                 |

## Ph.D. (2012-2016: IIT Indore)

**Thesis title:** “Fabrication and Optoelectronic Properties of Silicon Nanostructures” which includes

- Fabrication of well aligned silicon nanowires by Metal Induced Etching technique
- Effect of doping level and type (n & p-type) of silicon wafers on the formation of silicon nanowires by Metal Induced Etching

- Synthesis of various metal nano particles (silver gold and platinum)
- Surface morphology of nanostructures by SEM and AFM study
- Investigation of size dependent phonon confinement effect by Raman line-shape analysis: Experimental and Theoretical study
- Study of electron-phonon (Fano) interaction using Raman spectroscopy
- Study of interplay between phonon confinement and Fano effect using Raman spectroscopy
- Theoretical modeling to study interplay between phonon confinement and Fano effect in semiconductor nanostructures
- Understanding of origin of photoluminescence in silicon nanowires using diffuse reflectance and photoluminescence spectroscopy
- Application of well aligned silicon nanowires in field emission.

## Technical Skills

- **UV-Vis Spectrometers:**

1. Agilent Cary-60 with Diffuse Reflection Assembly.
2. Perkin UV-Vis.

- **Fluorescence Spectrometers:**

1. DongWoo Optron 80 K PL system.
2. Perkin Fluorescence Spectrometers LS 55.

- **Scanning Tunneling Microscope (STM):** Efficient in handling STM in various modes.
- **Lithography:** Experience on photo-lithography for patterning for microelectronics.
- **Raman Spectroscopy:** Efficient in handling various Raman spectrometers with different lasers having various wavelengths and powers.
- **Lasers:** Working experience on He-Cd lasers with 250 mW and low power He-Ne, and different diode lasers.
- **Other Fabrication and Characterization Techniques:** Atomic force microscopy (AFM), Metal Assisted Chemical Etching (MACE), spin coating system, microscopy, photoluminescence, Infra-red spectroscopy, and X-ray diffraction (powder and thin film), I-V measurements and four probe measurements.

## Other Skills/Training

- MS Windows, MS Office, ORIGIN, MATHCAD, COMSOL MultiPhysics, L<sup>A</sup>T<sub>E</sub>X, and different softwares used for various characterization machines.
- Three weeks workshop on Nano-sciences and Nano-technology in Grenoble at **France in 2015**
- One day workshop on “Laboratory Health and Safety Workshop” by Royal Society of Chemistry at Indian Institute of Technology Indore (**IIT**), Indore, India.
- Two days workshop on “Synchrotron Radiation” at Raja Ramanna Centre for Advanced Technology (**RRCAT**), Indore, India.

## Achievements & Awards

- Awarded **Postdoc Fellowship** at **National Institute for Nanotechnology, University of Alberta** Edmonton, Canada 2017.
- Awarded **National Postdoc Fellowship (NPDF) - SERB-DST** at **Indian Institute of Science (IISc.)** India April 2017. (not availed)
- Received fellowship from **SERB-DST** to attend the **International Conference on Advances in Functional Materials** in Jeju at **South Korea in 2016**.
- Received fellowship from **Indo-French Centre for the Promotion of Advance Research** to attend the **European School on Nano-sciences and Nano-technology** in Grenoble at **France in 2015**.
- Received fellowship from **Ministry of Human Resources and Development(MHRD)** to Pursue My Doctoral Study at **Indian Institute of Technology Indore, India** during the period 2012-2016.
- Qualified Graduate Aptitude Test in Engineering (GATE) in 2012; **All India Rank 736**.
- Qualified Joint Entrance Screening test (JEST), India in 2012; **All India Rank 553**
- Qualified CSIR-NET (LS) Examination Conducted by Council of Scientific & Industrial Research (CSIR), INDIA in December 2012 **All India Rank 173**.

## Publications

### In International Journals

1. Tefashe, U. M.; **Shailendra K. Saxena**; Colin Dick; McCreery, R. L. Unipolar Injection and Bipolar Light Emission in Ru-Centered Molecular Electronic Junctions. Accepted in J Phys Chem 2019
2. **Saxena, S.K.**, Smitt Scott R., Supur M., McCreery R.L.,: Light-stimulated Charge Transport in Bilayer Molecular Junctions (Accepted in Advanced Optical Materials July 2019 )

3. Tanwar, M., Chaudhary, A., Pathak, D.K., Yogi, P., **Saxena, S.K.**, Sagdeo, P.R., Kumar, R.: Deconvoluting Diffuse Reflectance Spectra for Retrieving Nanostructures' Size Details: An Easy and Efficient Approach. *J. Phys. Chem. A.* 123, 3607–3614 (2019). doi:10.1021/acs.jpca.9b01935
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5. Yogi, P., Tanwar, M., **Saxena, S.K.**, Mishra, S., Pathak, D.K., Chaudhary, A., Sagdeo, P.R., Kumar, R.: Quantifying the Short-Range Order in Amorphous Silicon by Raman Scattering. *Anal. Chem.* 90, 8123–8129 (2018)
6. Yogi, P., **Saxena, S.K.**, Chaudhary, A., Pathak, D.K., Mishra, S., Mondal, P., Joshi, B., Sagdeo, P.R., Kumar, R.: Porous Silicon's fractal nature revisited. *Superlattices Microstruct.* 120, 141–147 (2018)
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8. Tanwar, M., Yogi, P., Lambora, S., Mishra, S., **Saxena, S.K.**, Sagdeo, P.R., Krylov, A.S., Kumar, R.: Generalisation of phonon confinement model for interpretation of Raman line-shape from nano-silicon. *Adv. Mater. Process. Technol.* 4, 227–233 (2018)
9. Roy, S., Mishra, S., Yogi, P., **Saxena, S.K.**, Mishra, V., Sagdeo, P.R., Kumar, R.: Polypyrrole–vanadium oxide nanocomposite: polymer dominates crystallinity and oxide dominates conductivity. *Appl. Phys. A.* 124, 53 (2018)
10. Yogi, P., Poonia, D., Mishra, S., **Saxena, S.K.**, Roy, S., Kumar, V., Sagdeo, P.R., Kumar, R.: Spectral anomaly in Raman scattering from p-type silicon nanowires. *J. Phys. Chem. C.* 121, 5372–5378 (2017)
11. **Saxena, S.K.**, Yogi, P., Mishra, S., Rai, H.M., Mishra, V., Warshi, M.K., Roy, S., Mondal, P., Sagdeo, P.R., Kumar, R.: Amplification or cancellation of Fano resonance and quantum confinement induced asymmetries in Raman line-shapes. *Phys. Chem. Chem. Phys.* 19, 31788–31795 (2017)
12. **Saxena, S.K.**, Kumar, V., Rai, H.M., Sahu, G., Late, R., Saxena, K., Shukla, A., Sagdeo, P.R., Kumar, R.: Study of porous silicon prepared using metal-induced etching (MIE): a comparison with laser-induced etching (LIE). *Silicon.* 9, 483–488 (2017)
13. Roy, S., Mishra, S., Yogi, P., **Saxena, S.K.**, Sagdeo, P.R., Kumar, R.: Synthesis of conducting polypyrrole-titanium oxide nanocomposite: study of structural, optical and electrical properties. *J. Inorg. Organomet. Polym. Mater.* 27, 257–263 (2017)
14. Rai, H.M., Singh, P., **Saxena, S.K.**, Mishra, V., Warshi, M.K., Kumar, R., Rajput, P., Sagdeo, A., Choudhuri, I., Pathak, B., others: Room-temperature magneto-dielectric effect in  $\text{LaGaO}_3$ .  $7\text{FeO}$ .  $3\text{O}_3 + \gamma$ ; origin and impact of excess oxygen. *Inorg. Chem.* 56, 3809–3819 (2017)
15. Rai, H.M., **Saxena, S.K.**, Mishra, V., Kumar, R., Sagdeo, P.: Importance of frequency dependent magnetoresistance measurements in analysing the intrinsicity of magnetodielectric effect: A case study. *J. Appl. Phys.* 122, 054103 (2017)
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17. Mishra, S., Yogi, P., **Saxena, S.K.**, Jayabalan, J., Behera, P., Sagdeo, P., Kumar, R.: Significant field emission enhancement in ultrathin nano-thorn covered NiO nano-petals. *J. Mater. Chem. C.* 5, 9611–9618 (2017)

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21. Kumar, A., Warshi, M.K., Mishra, V., Saxena, S.K., Kumar, R., Sagdeo, P.R.: Strain control of Urbach energy in Cr-doped PrFeO<sub>3</sub>. *Appl. Phys. A*. 123, 576 (2017)
22. Yogi, P., **Saxena, S.K.**, Mishra, S., Rai, H.M., Late, R., Kumar, V., Joshi, B., Sagdeo, P.R., Kumar, R.: Interplay between phonon confinement and Fano effect on Raman line shape for semiconductor nanostructures: Analytical study. *Solid State Commun.* 230, 25–29 (2016)
23. Yogi, P., Mishra, S., Saxena, S.K., Kumar, V., Kumar, R.: Fano scattering: manifestation of acoustic phonons at the nanoscale. *J. Phys. Chem. Lett.* 7, 5291–5296 (2016)
24. **Shailendra K. Saxena**, R.K., Priyanka Yogi, Pooja Yadav, Suryakant Mishra, Haardik Pandey, Hari Mohan Rai, Vivek Kumar, Pankaj R. Sagdeo: Role of Metal Nanoparticles on porosification of silicon by metal induced etching (MIE). *Superlattices Microstruct.* 94, 101–107 (2016)
25. **Saxena, S.K.**, Borah, R., Kumar, V., Rai, H.M., Late, R., Sathe, V., Kumar, A., Sagdeo, P.R., Kumar, R.: Raman spectroscopy for study of interplay between phonon confinement and Fano effect in silicon nanowires. *J. Raman Spectrosc.* 47, 283–288 (2016)
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27. Rai, H.M., **Saxena, S.K.**, Mishra, V., Sagdeo, A., Rajput, P., Kumar, R., Sagdeo, P.: Observation of room temperature magnetodielectric effect in Mn-doped lanthanum gallate and study of its magnetic properties. *J. Mater. Chem. C*. 4, 10876–10886 (2016)
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34. Kumar, R., Sahu, G., **Saxena, S.K.**, Rai, H.M., Sagdeo, P.R.: Qualitative evolution of asymmetric raman line-shape for nanostructures. *Silicon.* 6, 117–121 (2014)

## Conference

1. **Saxena, S. K.**; Sahu, G.; Yogi, P.; Sagdeo, P. R.; Kumar, R. Spectroscopic Investigation of Well Aligned Silicon Nano Wires Fabricated by Metal Induced Etching. *Mater. Today Proc.* 2016, 3 (6), 1835–1839.
2. **Saxena, S. K.**; Sahu, G.; Sagdeo, P. R.; Kumar, R. Quantum Confinement Effect in Cheese like Silicon Nano Structure Fabricated by Metal Induced Etching. In *AIP Conference Proceedings*; AIP Publishing, 2015; Vol. 1675, p 030031.
3. **Saxena, S. K.**; Rai, H. M.; Late, R.; Sagdeo, P. R.; Kumar, R. Origin of Photoluminescence from Silicon Nanowires Prepared by Metal Induced Etching (MIE). In *AIP Conference Proceedings*; AIP Publishing, 2015; Vol. 1661, p 080027.
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5. Late, R.; Rai, H. M.; **Saxena, S. K.**; Kumar, R.; Sagdeo, P. Effect of Hafnium Substitution on the Dielectric Properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . In *AIP Conference Proceedings*; AIP Publishing, 2015; Vol. 1665, p 140019.

## References

Dr. Rajesh Kumar  
Associate Professor and Dean (Planning)  
Discipline of Physics  
Indian Institute of Technology Indore  
Email : [rajeshkumar@iiti.ac.in](mailto:rajeshkumar@iiti.ac.in)  
Phone(O): +91731-2438901

Prof. Richard L. McCreery  
Professor  
Department of Chemistry  
University of Alberta, Edmonton AB  
Canada T6G 2N4  
Email: [mccreery@ualberta.ca](mailto:mccreery@ualberta.ca)  
Phone(O): +1-780-492-9594

Dr. P C Mondal  
Department of Chemistry  
Indian Institute of Technology Kanpur  
Email: [pcmondal@iitk.ac.in](mailto:pcmondal@iitk.ac.in)

Dr. Abhishek Srivastava  
Assistant Professor and Dean of Student Affairs  
Discipline of Computer Science and Engineering  
Indian Institute of Technology, Indore  
Email : [asrivastava@iiti.ac.in](mailto:asrivastava@iiti.ac.in) Phone(O): +91731-2438901

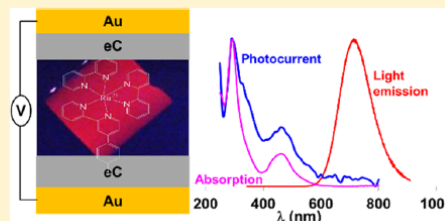
Prof. V.D. Vankar Professor  
Department of Physics  
Indian Institute of Technology Delhi  
Email : [vdvankar@physics.iitd.ac.in](mailto:vdvankar@physics.iitd.ac.in)  
Phone(O): +9111-26591329 .

## Unipolar Injection and Bipolar Transport in Electroluminescent Ru-Centered Molecular Electronic Junctions

Ushula M. Tefashe,<sup>†</sup> Colin Van Dyck,<sup>‡</sup> Shailendra K. Saxena,<sup>†</sup> Jean-Christophe Lacroix,<sup>§</sup> and Richard L. McCreery<sup>\*,†</sup><sup>†</sup>Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta T6G 2G2, Canada<sup>‡</sup>Department of Physics, University of Mons, 20, place du Parc, 7000 Mons, Belgium<sup>§</sup>University de Paris, ITODYS, CNRS UMR 7086, 15 rue J-A de Baif, F-75013 Paris, France

## Supporting Information

**ABSTRACT:** Bias-induced light emission and light-induced photocurrents were used as independent probes of charge transport in carbon-based molecular junctions containing Ru(bpy)<sub>3</sub>. The thickness, bias, and temperature dependence of both the total device current and photoemission were compared, as well as their response to bias pulses lasting from a few milliseconds to several seconds. The device current was exponentially dependent on the square root of the applied electric field, with weak dependence on thickness when compared at a constant field. In contrast, light emission was strongly dependent on thickness at a given electric field, with a thickness-independent onset for light emission and a large intensity increase when the bias exceeded the 2.7 V HOMO–LUMO gap of Ru(bpy)<sub>3</sub>. The apparent activation energies for light emission and current were similar but much smaller than those expected for thermionic emission or redox exchange. Light emission lagged current by several milliseconds but reached maximum emission in 5–10 ms and then decreased slowly for 1 s, in contrast to previously reported solid-state Ru(bpy)<sub>3</sub> light-emitting devices that relied on electrochemical charge injection. We conclude that at least two transport mechanisms are present, that is, “unipolar injection” initiated by electron transfer from a Ru(bpy)<sub>3</sub> HOMO to the positive electrode and “bipolar injection” involving hole and electron injection followed by migration, recombination, and light emission. The unipolar mechanism is field-driven and the majority of the device is current, while the bipolar mechanism is bias-driven and involves electrode screening by PF<sub>6</sub> ions or mobile charges. In addition, significant changes in thickness and temperature dependence for thicknesses exceeding 15 nm imply a change from injection-limited transport to bulk-limited transport. The current results establish unequivocally that electrons and holes reside in the molecular layer during transport once the transport distance exceeds the ~5 nm limit for coherent tunneling and that redox events involving nuclear reorganization accompany transport. In addition, they demonstrate luminescence in a single organometallic layer without hole or electron transport layers, thicknesses below 30 nm, and symmetric electrodes with similar work functions.



## INTRODUCTION

The field of molecular electronics investigates charge transport in mainly organic molecules across distances ( $d$ , nm) as short as one molecule (~1 nm) up to ~30 nm, motivated in part by the ability to modify transport and electronic properties by changes in molecular structure, sometimes dubbed “rational design”. Transport mechanisms over 1–30 nm may involve tunneling and other mechanisms that differ fundamentally from those reported for the >50 nm distances commonly encountered in thin-film transistors<sup>1–5</sup> and organic light-emitting diodes (OLEDs)<sup>6–8</sup> widely studied in the field of organic electronics. Many studies of single molecule and “ensemble” molecular junctions (MJs) have concluded that quantum mechanical tunneling is the dominant mechanism for aliphatic molecules with  $d < 2$  nm or conjugated molecules with  $d < 5$  nm. For  $d > 5$  nm and aromatic molecules, a transition from tunneling to a different, often activated mechanism has been reported and attributed to resonant

transport,<sup>9–11</sup> field ionization,<sup>12</sup> Schottky injection,<sup>13</sup> and hopping mediated by activated, Marcus-like polaron transport between subunits in an oligomer.<sup>14,15</sup> Transport in some cases with  $d > 5$  nm is temperature-dependent, with apparent activation energies ( $E_{\text{act}}$ ) of 200–300 meV,<sup>14,15</sup> while other examples exhibit  $E_{\text{act}} < 100$  meV over a range of 200–300 K or are activationless, with  $E_{\text{act}}$  being statistically zero below 200 K.<sup>11,12,16,17</sup> In the case of bis-thienyl benzene oligomers between carbon electrodes, current densities exceeding 10 A/cm<sup>2</sup> were observed across 22 nm and  $T < 10$  K when the applied bias exceeded 5 V.<sup>12</sup>

Molecular junctions with  $d$  in the range of 2–40 nm, which contain metal centers (Ru, Co, Fe, etc.), are of interest to charge transport mechanisms due to redox levels, which may

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# Light-Stimulated Charge Transport in Bilayer Molecular Junctions for Photodetection

Shailendra K. Saxena, Scott R. Smith, Mustafa Supur, and Richard L. McCreery\*

Eleven bilayer molecular junctions (MJs) consisting of two different 5–7 nm thick molecular layers between conducting contacts are investigated to determine how orbital energies and optical absorbance spectra of the oligomers affect the photocurrent (PC) response, the direction of photoinduced charge transport, and maximum response wavelength. Photometric sensitivity of  $2 \text{ mA W}^{-1}$  and a detection limit of 11 pW are demonstrated for MJs, yielding an internal quantum efficiency of 0.14 electrons per absorbed photon. For unbiased MJs, the PC tracks the absorption spectrum of the molecular layer, and is stable for >5 h of illumination. The organic/organic (O/O) interface between the molecular layers within bilayer MJs is the primary determinant of PC polarity, and the bilayer MJ mechanism is conceptually similar to that of a single O/O heterojunction studied in bilayers of much greater thickness. The charge transport direction of the 11 MJs is completely consistent with hole-dominated transport of photogenerated carriers. For MJs illuminated while an external bias is applied, the PC greatly exceeds the dark current by factors of  $10^2$  to  $10^5$ , depending on bias, bilayer structure, and wavelength. The bilayer MJs are amenable to flexible substrates, and may have applications as sensitive, wavelength-specific photodetectors.

## 1. Introduction

Stimulation of charge transport by incident light has long been studied and exploited in both inorganic and organic semiconductors, with familiar examples being the charge-coupled device, photodiodes, photocells, and light-emitting diodes. For organic semiconductors such as thin-film transistors and organic photovoltaic devices, transport distances generally exceed 50 nm since spin coating is a common fabrication technique. When the charge transport distances in organic electronic devices are below  $\approx 15$  nm, the realm of molecular electronics emerges, with often very different transport mechanisms such as coherent tunneling<sup>[1]</sup> and field ionization.<sup>[2]</sup> Molecular junctions (MJs) consisting of single molecules or arrays of parallel molecules between conducting contacts have


been studied extensively.<sup>[1,3]</sup> The field is driven in part by the possibility of new electronic functions in molecular devices and the wide variety of molecular structures available, presumably with a broad range of electronic behaviors.<sup>[4]</sup> “Large area” or “ensemble” MJs with partially transparent contacts enable the use of optical spectroscopy for characterization and monitoring of molecular electronic devices using infrared absorption,<sup>[5]</sup> Raman,<sup>[6]</sup> and UV-vis spectroscopy.<sup>[4d,7]</sup>

While optical spectroscopy is normally a probe of device structure during fabrication and operation, the field of “molecular optoelectronics” investigates stimulation of transport with light or generation of light in response to an external bias.<sup>[8]</sup> Photocurrent (PC) generation and changes in MJ conductance by incident light have been reported for single molecules and molecular ensembles and examined theoretically.<sup>[4a,9]</sup> We have reported PCs and photoconductance changes in carbon-based MJs, mediated by internal photoemission (IPE)<sup>[10]</sup> and optical absorption in the

molecular layer.<sup>[11]</sup> The observed PC tracks the in situ UV-vis absorption spectrum of the molecular layer when the transport distance exceeds 5 nm, and the PC polarity (i.e., the charge transport direction) and induced photovoltage correlate strongly with which orbitals mediate transport (highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO)).<sup>[11b]</sup> Carbon-based MJs also exhibit photoemission from hot electrons,<sup>[8c,12]</sup> and transport in thiol-based large-area MJs can couple to plasmons in the contacts to emit light.<sup>[8d,13]</sup>

For PCs in unbiased, Au/carbon/molecule/carbon/Au MJs with identical top and bottom electrodes, the direction of illumination did not cause a change in PC sign, indicating that there must be some inherent asymmetry in the device. We attributed the asymmetry in single-component carbon-based MJs to a difference in electronic coupling at the two electrode contacts, one of which is covalent and the other physisorbed.<sup>[11b]</sup> This effect was predicted theoretically by Galperin et al.<sup>[8b,14]</sup> Since the internal electric field generated by the effect is small (10–30 mV), the resulting PCs are also small for single-component MJs, and would likely be absent if the electronic coupling to both electrodes were identical. We recently reported a different approach in which a molecular bilayer was used to create asymmetry, leading to significantly larger PCs.<sup>[15]</sup> Successive reduction of two diazonium reagents<sup>[16]</sup> resulted in a covalent

Dr. S. K. Saxena, Dr. S. R. Smith, Dr. M. Supur, Prof. R. L. McCreery  
Department of Chemistry  
University of Alberta  
11227 Saskatchewan Dr., Edmonton, Alberta T6G 2G2, Canada  
E-mail: richard.mccreery@ualberta.ca

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adom.201901053>.

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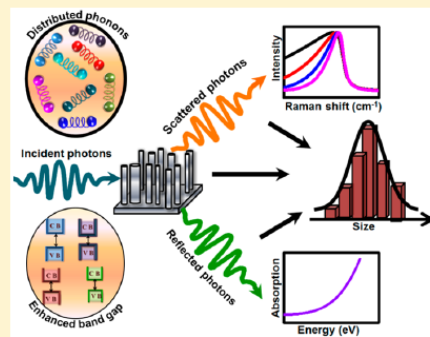
# Deconvoluting Diffuse Reflectance Spectra for Retrieving Nanostructures' Size Details: An Easy and Efficient Approach

Manushree Tanwar, Anjali Chaudhary,<sup>1</sup> Devesh K. Pathak, Priyanka Yogi,<sup>2</sup> Shailendra K. Saxena,<sup>3</sup> Pankaj R. Sagdeo,<sup>4</sup> and Rajesh Kumar<sup>1\*</sup>

Material Research Laboratory, Discipline of Physics & MEMS, Indian Institute of Technology Indore, Simrol 453552, India

## Supporting Information

**ABSTRACT:** A new model has been reported here to estimate the mean size and size distribution in nanostructured materials by utilizing a simple and economic diffuse reflectance spectroscopy through spectral line-shape analysis. In the proposed model, a theoretical line shape has been derived by taking into account a size distribution function, which represents a variation in absorption coefficient as a function of size, which in turn depends on the band gap and thus on the excitation photon energy. A fitting of the experimental absorption spectra with the derived line-shape function yields the mean crystallite size and size distribution. The size and size distribution have been successfully estimated from two different silicon nanostructured samples, prepared by metal induced etching. The model has been validated by comparing the estimated values with the sizes estimated using Raman spectroscopy, which is a well-known technique. The two results are not only consistent with each other but are also found to be consistent with the electron microscopy's results, revealing that a technique as simple and as economic as diffuse reflectance spectroscopy can be used to estimate size distribution. In addition, the proposed model can also be used to investigate the homogeneity in the size distribution in a nanostructured sample.



## INTRODUCTION

For more than three decades now, the perturbed physical and chemical properties of materials including semiconductors due to size effect (quantum confinement) have gained massive attention and inquisitiveness for the exploration of these materials in devices for different applications like field emission,<sup>1,2</sup> batteries,<sup>3</sup> solar cell,<sup>4</sup> sensors,<sup>5,6</sup> capacitors,<sup>7</sup> etc. With new applications of nanomaterials comes the challenge to characterize them. For applications where size-dependent properties<sup>8–12</sup> are explored it becomes very critical to have precise information about not only the size but also the size distribution (SD) if there is any. Among various methods to estimate the size of nanostructures, electron microscopy is the only direct method with a limitation to predict the size of nanostructures only in a very small area on the sample. Other indirect methods utilized for this purpose are many including Raman spectroscopy, dynamic light scattering,<sup>13</sup> etc. Raman spectroscopy is a very versatile tool but a bit expensive whereas the dynamic light scattering needs a particular type of sample preparation. A given method has its own advantages and disadvantages; thus, it is very difficult to conclude the true picture. Thus, an alternate easy and efficient method is the need of the hour, which can predict the size and SD of nanostructures. While exploring the new ways, it is important to understand the relationship between the size (and SD) and a given observable of the experiment which is size-dependent phonon frequency shift in case of Raman spectra and correlation spectroscopy for dynamic light scattering as

examples. Dependence of band gap on size is a known phenomenon and thus its implication on the absorption and/or reflectance (for nontransparent samples) spectra is expected. In other words, the absorption spectrum contains the information on size and SD present in the sample which is manifested in terms of the deviation from the typically observed ideal spectra from a bulk material. If this relationship is understood properly, a careful analysis of the absorption spectra may, in principle, be used to estimate the size and SD for a given nanostructures samples. The same has been explored in the current study by taking the example of silicon (Si) nanowires (NWs).

Silicon when confined to one dimension (NWs) shows interesting perturbations in its optoelectronic, and several other, properties, which allows one to use it as a suitable material to be explored in distinct device applications. There are various fabrication techniques involved for nanostructure fabrication including bottom-up techniques like vapor–solid–liquid growth<sup>14</sup> and molecular beam epitaxy<sup>15</sup> and top-down techniques like pulsed laser ablation,<sup>16</sup> ion beam etching,<sup>17</sup> and metal assisted chemical etching popularly known metal induced etching.<sup>18–21</sup> In the present study, metal induced etching has been used to fabricate SiNWs from an n- and a p-type Si wafer because metal induced etching is one of the

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# Precursor concentration dependent hydrothermal NiO nanopetals: Tuning morphology for efficient applications



Devesh K. Pathak, Anjali Chaudhary, Suryakant Mishra<sup>2</sup>, Priyanka Yogi, Shailendra K. Saxena<sup>1</sup>, P.R. Sagdeo, Rajesh Kumar\*

Material Research Laboratory, Discipline of Physics & MEMS, Indian Institute of Technology Indore, Simrol, 453552, India

## ABSTRACT

A precursor's concentration dependent surface morphologies of NiO nanopetals (NPs) have been studied for designing application-specific nanomaterials by hydrothermal technique. The surface morphologies, obtained using scanning electron microscopy, have been analysed using ImageJ to extract information about the dependence of petal thickness, petal density and linear porosity on the concentration at a given deposition and annealing temperatures. A detailed analysis shows how the synthesis parameters can be optimized to get a desired application specific nanostructure by taking an example of field emission properties. NiO NPs were prepared with three different precursor's concentrations out of which the sample prepared with lowest concentration was identified to show very good field emission property with high enhancement factor.

## 1. Introduction

Enormous research in fields related to nanomaterials [1,2] are being carried out globally and constantly expanding its applicability in nanoscience and nanotechnology [2–5]. The research in the nanotechnology includes various aspects of functional nanomaterials including fabrication methods [6] as it involves the quality and cost of the end product. Optimization of various fabrication parameters [7], affecting the nanomaterials' properties, can be considered as one of the most important steps as it decides the material onto which the performance of the end device will depend. Different nanomaterials' morphologies are obtained when prepared by different synthesis methods [8,9]. This is mainly because the synthesis method and associated atomistic dynamics decide how they will come together to result in the nano-form under a given thermodynamic conditions which in turn gets directly manifested in a unique morphology [10]. In other words, morphological variation can be one of the best parameters to study the property of nanostructure thus helping one in identifying best suitable material for applications. The morphology can be controlled by appropriately choosing the parameters and may result in surface architecture, tuned for a particular cause.

Nanoscaled materials are being widely used for variety of applications in science, engineering and biomedical fields for energy generation & storage [11], electrochromic display [12], sensing application [13], diagnostic & therapeutics [14] etc. Materials, which are of current interest, include metal oxides due to their applications in various devices mentioned above. Nickel oxide (NiO), has drawn attention in recent years due to its dielectric properties attributed to its wide band gap [15]. Recently NiO has been widely studied for applications [16–20] in electrochromism [21], sensing, and transparent conducting electrodes [22,23]. Its multilayer mesoporous films show excellent electrochemical capacitance properties [24]. Recent morphology dependent field emission from NiO NSs has received good response amongst researchers to explore it further.

Nanomaterials' fabrication methods are plenty including hydrothermal method [8], pulse laser deposition [25], electrodeposition

\* Corresponding author.

E-mail address: [rajeshkumar@iiti.ac.in](mailto:rajeshkumar@iiti.ac.in) (R. Kumar).

<sup>1</sup> Present address: National Institute for Nanotechnology, University of Alberta, Edmonton, Canada.

<sup>2</sup> Present address: Department of Chemical and Biological Physics, Weizmann Institute of Science, Rehovot 76100, Israel.

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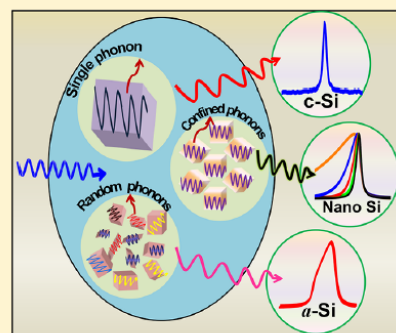
# Quantifying the Short-Range Order in Amorphous Silicon by Raman Scattering

Priyanka Yogi,<sup>†</sup> Manushree Tanwar,<sup>†</sup> Shailendra K. Saxena,<sup>\*,‡,§</sup> Suryakant Mishra,<sup>§</sup> Devesh K. Pathak, Anjali Chaudhary, Pankaj R. Sagdeo,<sup>||</sup> and Rajesh Kumar<sup>\*,||</sup>

Material Research Laboratory, Discipline of Physics & MEMS, Indian Institute of Technology Indore, Simrol-453552, India

## Supporting Information

**ABSTRACT:** Quantification of the short-range order in amorphous silicon has been formulated using Raman scattering by taking into account established frameworks for studying the spectral line-shape and size dependent Raman peak shift. A theoretical line-shape function has been proposed for representing the observed Raman scattering spectrum from amorphous-Si based on modified phonon confinement model framework. While analyzing modified phonon confinement model, the term “confinement size” used in the context of nanocrystalline Si was found analogous to the short-range order distance in a-Si thus enabling one to quantify the same using Raman scattering. Additionally, an empirical formula has been proposed using bond polarizability model for estimating the short-range order making one capable to quantify the distance of short-range order by looking at the Raman peak position alone. Both the proposals have been validated using three different data sets reported by three different research groups from a-Si samples prepared by three different methods making the analysis universal.



Nanoscience and nanotechnology has been established as an important area, which makes it equally important to characterize these materials which were considered amorphous for long.<sup>1,2</sup> At the junction of the (poly-)crystalline and amorphous, in a particular crystallite size window,<sup>3,4</sup> a size-dependent property variation was observed, which marks the domain of the nanoscience.<sup>5,6</sup> The length of ordered material<sup>7</sup> (in the crystallinity) remained the distinguishing parameter between the three phases of solid,<sup>8</sup> crystalline,<sup>9,10</sup> nanocrystalline,<sup>11</sup> and amorphous,<sup>12</sup> with crystalline material having the longest range of order of crystallinity, whereas amorphous material<sup>13</sup> has the least. The distance up to which a (poly-)crystalline solid maintains the crystallinity defines the degree of order,<sup>14</sup> which is quantified by the crystallite size. Though the crystallite size quantifies the degree of order in crystalline materials, ambiguity remains inherently, while quantifying the term in amorphous material as the range of the order is rather “short” and usually not defined even empirically. Whereas, in nanocrystalline materials the crystallite size comparable to the Bohr’s radius<sup>15,16</sup> declares the onset of the “nano” regime and can be defined as the distance of the range of order. Such kind of quantification of the degree of order may prove to be of scientific and technological importance and thus needs attention. As an example, it is often observed that efficiency of amorphous silicon (a-Si) solar cells<sup>17,18</sup> depends on the method of material preparation though the actual player responsible for this variation is unknown. It is possible to see a correlation between the quantified short-range order and solar cell efficiency thus will be helpful in designing an appropriate a-

Si device. Additionally, quantification of the short-range order in amorphous materials may help in identifying any possible scientific information in this gray area, which may lead to great discoveries as in the case of nanoscience.

Presence of order, whether short-range or long-range, can be examined by X-ray diffraction (XRD) qualitatively but can not be quantified by this method. Raman scattering,<sup>19–21</sup> which has been established as a widely used versatile spectroscopic tool, may prove to be just appropriate for the purpose because of its various scientific merits. The only disadvantage, being a weak phenomenon, has been taken care of in the instrumentation because of the availability of very good source and detectors making it an unmatched characterization tool used by scientists across all the disciplines. Raman scattering is not only a probe to study the phase identification,<sup>22,23</sup> chemical compositions,<sup>24,25</sup> and level of doping<sup>26,27</sup> but it also has shown a promising potential for acting as a sensitive probe to monitor various physical phenomena taking place at microscopic levels, such as confinement,<sup>21,28–31</sup> defect structures, and crystalline nature of materials.<sup>32</sup> Because of its immense advantages and broader acceptability, Raman spectroscopy has not lagged behind even in understanding different phenomena in comparatively newer but exceptionally important field of nanosciences and nanotechnology.<sup>33,34</sup> At times, Raman spectroscopy has been proved to be superior to other methods

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