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Probing C84-embedded Si substrate using scanning probe microscopy and molecular dynamics

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Abstract:	This paper reports an array-designed C84-embedded Si substrate fabricated using a controlled self-assembly method in an ultra-high vacuum chamber. The characteristics of the C84-embedded Si surface, such as atomic resolution topography, local electronic density of states, band gap energy, field emission properties, nanomechanical stiffness, and surface magnetism, were examined using a variety of surface analysis techniques under UHV conditions as well as in an atmospheric system. Experimental results demonstrate the high uniformity of the C84-embedded Si surface fabricated using a controlled self-assembly nanotechnology mechanism, represents an important development in the application of FED, optoelectronical device fabrication, MEMS cutting tools, and in efforts to find a suitable replacement for carbide semiconductors. Molecular dynamics (MD) method with semi-empirical potential can be used to study the nanoindentation of C84-embedded Si substrate. A detailed description for performing MD simulation is presented here. Details for a comprehensive study on mechanical analysis of MD simulation such as indentation force, Young's modulus, surface stiffness, atomic stress, and atomic strain are included. The atomic stress and von-Mises strain distributions of the indentation model can be calculated to monitor deformation mechanism with time evaluation in atomistic

	level.
Author Comments:	Dear Editor, Thank you for your interest in our research and invite us to submit our research protocol to your journal. We are pleased to submit our manuscript entitled "Probing C84-embedded Si substrate using scanning probe microscopy and molecular dynamics" for your kind consideration for publication in the "Journal of Visualized Experiments" as an article. The following is a brief description of the work and why we think it merits publication in this journal. It is well known that the SiC has a wide bandgap semiconductor with extreme properties such as wear/corrosion resistivity, high breakdown field, high current density and high thermal conductivity, which make it a promising material for device applications that are integral to high-temperature, high-power circuit elements. In recent year, C84 molecules can be further embedded into a silicon substrate surface and form a hexagonal closed-packed array on the silicon substrate, which has been found to serve as a successor to silicon carbide materials. In the present article, the protocol shows the fabrication of a C84-embedded Si substrate heterojunction and subsequent analysis to obtain a comprehensive understanding of the electronic, optoelectronic, mechanical, magnetic, and field emission properties of the resulting materials. We also addressed the issue of using numerical simulation to predict the characteristics of nanomaterials, through the novel application of molecular dynamics calculations. We certify that this is an original work that has not been submitted elsewhere for publication. We hope that our manuscript meets the high standards of your journal. We are looking forward to receiving a favorable response from your regarding the acceptance of our manuscript. Thank you for your time and consideration. Sincerely yours, Wen-Jay Lee
Additional Information:	
Question	**Response**
If this article needs to be "in-press" by a certain date to satisfy grant requirements, please indicate the date below and explain in your cover letter.	

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Re: "*Probing C84-embedded Si substrate using scanning probe microscopy and molecular dynamics*", by Mon-Shu Ho, Chih-Pong Huang, Che-Fu Chou, Wen-Jay Lee

Dear Editor

Thank you for your interest in our research and invite us to submit our research protocol to your journal. We are pleased to submit the above titled manuscript for your kind consideration for publication in the "*Journal of Visualized Experiments*" as an article. The following is a brief description of the work and why we think it merits publication in this journal.

It is well known that the SiC has a wide bandgap semiconductor with extreme properties such as wear/corrosion resistivity, high breakdown field, high current density and high thermal conductivity, which make it a promising material for device applications that are integral to high-temperature, high-power circuit elements. In recent year, C84 molecules can be further embedded into a silicon substrate surface and form a hexagonal closed-packed array on the silicon substrate, which has been found to serve as a successor to silicon carbide materials.

In the present article, the protocol shows the fabrication of a C84-embedded Si substrate heterojunction and subsequent analysis to obtain a comprehensive understanding of the electronic, optoelectronic, mechanical, magnetic, and field emission properties of the resulting materials. We also addressed the issue of using numerical simulation to predict the characteristics of nanomaterials, through the novel application of molecular dynamics calculations.

We certify that this is an original work that has not been submitted elsewhere for publication. We hope that our manuscript meets the high standards of your journal. We are looking forward to receiving a favorable response from your regarding the acceptance of our manuscript. Thank you for your time and consideration.

Sincerely yours,

Wen-Jay Lee

TITLE:
Probing C_{84}-embedded Si substrate using scanning probe microscopy and molecular dynamics.

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KEYWORDS:
Fullerene, C_{84}, Si substrate, electronics, surface magnetism, molecular dynamics, scanning probe microscopy, nanomechanics, mechanical property, nanoindentation

SHORT ABSTRACT:
This paper reports the nanomaterial fabrication of a fullerene Si substrate inspected and verified by nanomeasurements and molecular dynamic simulation.

LONG ABSTRACT:

This paper reports an array-designed C_{84}-embedded Si substrate fabricated using a controlled self-assembly method in an ultra-high vacuum chamber. The characteristics of the C_{84}-embedded Si surface, such as atomic resolution topography, local electronic density of states, band gap energy, field emission properties, nanomechanical stiffness, and surface magnetism, were examined using a variety of surface analysis techniques under ultra, high vacuum (UHV) conditions as well as in an atmospheric system. Experimental results demonstrate the high uniformity of the C_{84}-embedded Si surface fabricated using a controlled self-assembly nanotechnology mechanism, represents an important development in the application of field emission display (FED), optoelectronical device fabrication, MEMS cutting tools, and in efforts to find a suitable replacement for carbide semiconductors. Molecular dynamics (MD) method with semi-empirical potential can be used to study the nanoindentation of C_{84}-embedded Si substrate. A detailed description for performing MD simulation is presented here. Details for a comprehensive study on mechanical analysis of MD simulation such as indentation force, Young's modulus, surface stiffness, atomic stress, and atomic strain are included. The atomic stress and von-Mises strain distributions of the indentation model can be calculated to monitor deformation mechanism with time evaluation in atomistic level.

INTRODUCTION:

Fullerene molecules and the composite materials they comprise are distinctive among nanomaterials due to their excellent structural characteristics, electronic conductivity, mechanical strength, and chemical properties[1-4]. These materials have proven highly beneficial in a range of fields, such as electronics, computers, fuel cell technology, solar cells, and field emission technology[5,6].

Among these materials, silicon carbide (SiC) nanoparticle composites have received particular attention thanks to their wide band gap, high thermal conductivity and stability, high electrical breakdown ability, and chemical inertness. These benefits are particularly obvious in optoelectronic devices, metal-oxide-semiconductor field-effect transistors (MOSFET), light-emittingdiodes (LEDs), and high-power, high-frequency, and high-temperature applications. However, high density defects commonly observed on the surface of conventional silicon carbide can have detrimental effects on the electronic structure, even leading to device failure[7,8]. Despite the fact that the application of SiC has been studied since 1960, this particular unresolved problem remains.

The aim of this study was the fabrication of a C_{84}-embedded Si substrate heterojunction and subsequent analysis to obtain a comprehensive understanding of the electronic, optoelectronic, mechanical, magnetic, and field emission properties of the resulting materials. We also addressed the issue of using numerical simulation to predict the characteristics of nanomaterials, through the novel application of molecular dynamics calculations.

PROTOCOL:

Note: The paper outlines the methods used in the formation of a self-assembled fullerene array on the surface of a semiconducting substrate. Specifically, we present a novel method for the preparation of a fullerene-embedded silicon substrate for use as a field emitter or substrate in microelectromechanical systems(MEMS), and optoelectronic devices in high-temperature, high-power, applications as well as in high-frequency devices [9-13].

1. Fabrication of hexagonal-closed-packaged (HCP) overlayer of C_{84} on Si substrate

1.1) Prepare clean Si (111) substrate

1.1.1) Subject Si substrate to RCA (Radio Corporation of America) cleaning, involving the application of a solvent followed by heating in an ultra-high vacuum system for the removal of the oxide layer and impurities from the surface of the substrate (see supporting material).

Note: Herein, the term “UHV-ultra high vacuum system” refers to a vacuum below 1 x 10^{-8} Pa used in the preparation of a Si(111).

1.2) Deposit C_{84} on silicon surface using thermal evaporation in a UHV system

1.2.1) Pre-heat a K-cell evaporator with external power supply through heating filaments to 500 ^{o}C to promote the outgassing of impurities.

1.2.2) Load C_{84} nanoparticles into a K-cell container. Resistively heat the K-cell to 650 ^{o}C. Vaporize C_{84} nanoparticles as C_{84} nanoparticles in the container compose vapors. Evaporate C_{84} nanoparticles in straight lines until nanoparticles strike a Si substrate through a controlled valve at pressure below 5X10^{-8} Pa.

1.3) Embed C_{84} molecules within Si surface via self-assembly mechanism

1.3.1) Pre-anneal Si(111) substrate in an ultra-high vacuum system at 900 ^{o}C to obtain (1x1) structures. Reduce the temperature to 650 ^{o}C for 30 min for the deposition of the C_{84} nanoparticles on the surface of the substrate.

1.3.2) Anneal the Si substrate at ~750 ^{o}C for 12 hours, during which time the powdered-C_{84} nanoparticles self-assemble into a highly uniform fullerene array on the surface of the Si(111) substrate.

Note: Herein, the term “highly uniform fullerene array” refers to the uniform distribution of fullerene on the substrate, in which most of the nanoparticles are oriented in a compact arrangement perpendicular to the surface of the substrate. This configuration helped to ensure that the vertical height of the fullerene array was essentially identical in all samples.

2. Measurements of Electronic Properties of C_{84}-embedded Si substrate

2.1) Measure local electronic density of states using UHV-scanning tunneling microscopy

2.1.1) Measure I-V curves of specific atoms using UHV-SPM

2.1.2) Place C_{84}-embedded Si substrate on a SPM sample holder. Introduce the holder into an UHV-STM (scanning tunneling microscope) scanning head system. Sweep applied sample bias from -5V to 5V.

2.1.3) Click on "**I-V**" measurement item to measure the tunneling current **I** at atomic resolution. Choose at least 20 particular locations on the C_{84}-embedded Si substrate for measurements. Calculate the mean value of tunneling current I over 20 particular locations. Derive I as a function of voltage. Plot I-V curves.

2.1.4) Calculate the derivative of I(V) with respect to V. Convert the I-V curves to dI/dV as a function of voltage in order to determine the local electronic state of the C_{84}-embedded Si substrate.

2.2) Measure band gap energy

2.2.1) Obtain I-V curves according to the procedures in 2.1.2 and 2.1.3 from the following: Si(111)-7x7 surface, Si(111)-1x1 surface, single individual C_{84} nanoparticles on Si, 7-19 C_{84} clusters on Si, 20-50 C_{84} clusters on Si, and a monolayer of C_{84} embedded within Si surface.

2.2.2) Calculate the derivative of I(V) with respect to V. Convert the I-V curves to dI/dV curves to measure the HOMO-LUMO energy differences (referred to band gap energy) in each measurement location, as shown in Figure 2(a).

2.3) Obtain field emission (FE) properties

2.3.1) Place C_{84}-embedded Si substrate on a FE sample holder. Insert the holder into FE analysis chamber. Evacuate the chamber to a pressure of approximately 5 $\times 10^{-5}$ Pa for FE measurement. Note: The C_{84}-embedded silicon substrate functioned as the cathode and a copper probe with a cross-sectional area of ~0.71 mm^2 functioned as the anode. The distance between the cathode and anode was approximately 590 µm.

2.3.2) Increase applied voltage manually on substrate from 100V to 1100V. Measure the corresponding field emission current as a function of applied voltage using a high-voltage source measurement unit with current amplifier.

2.3.3) Calculate the Fowler-Nordheim field emission correlation according to the work function ~ 5eV as shown in Figure 2(b).

2.3.4) Obtain the geometric field enhancement factor (β) as follows: F(field)= β(V/d) with a β value of approximately 4383.

2.3.5) Obtain the electrical breakdown field under vacuum based on the slope of the natural logarithm (J/E^2) vs ($1/E$), which gave us a value of ~$4.0x10^6$ V/cm for the C_{84}-embedded Si substrate as shown in Figure 2(c).

2.4) Optoelectronic properties

2.4.1) Transfer testing substrate to an optical emission measurement system. Focus a He–Cd laser source with 325 nm emissions on the substrate that is located in the center of the sample compartment. Set up a spectrometer in a suitable position. Use a spectrometer to acquire the photoluminescence spectrum by collecting and analyzing emitting photons. The optoelectronic result is shown in Figure 2(d).

3.Measurements of surface magnetism

3.1) Obtain MFM (magnetic force microscopy) topography.

3.1.1) Magnetize samples of C_{84}-embedded Si prior to MFM measurements by applying a magnet with a field strength of approximately 2 kOe.

3.1.2) Place the magnetized sample on an MFM sample stage. Click on "Obtain MFM topography" item. Observe the microstructure of the fullerene in the magnetic domain embedded within the Si substrate using MFM in lift mode with the application of magnetization perpendicular to the surface of the sample.

3.1.3) Use a nano-scale PPP-MFMR cantilever for MFM measurements (Figure 3 (a)). Determine the surface magnetism if MFM topography appears darker(brighter) when the magnetic moment of tip is in the same(opposite) direction of the substrate moment.

3.2) SQUID (superconducting quantum interference device) measurement

3.2.1) Prepare monolayer of C_{84}-embedded Si substrate and C_{84} clusters on C_{84} embedded Si substrate.

3.2.2) Magnetize samples of C_{84}-embedded Si and C_{84} clusters on C_{84} embedded Si substrate prior to SQUID experiments by applying a magnet with a field strength of approximately 2 kOe.

3.2.3) Place the sample in an SQUID. Apply a sweeping magnetic field in a range of ~ 2 kOe. Obtain the magnetization loops plotted versus the external magnetic field in SQUID measurements at room temperature. Note: The typical M-H curve for a ferromagnetic material can be obtained as shown in Figure 3(b).

4.Measurement of nanomechanical properties by AFM

Note: Atomic force microscopy (AFM) provides a powerful tool for the characterization of material and mechanical properties at the micro- and nano-scales in air as well as in a UHV environment

4.1) Measure the stiffness of C_{84} embedded Si substrate under atmospheric conditions

4.1.1) Place the substrate on an AFM sample stage. Drag a sharp tip over the substrates using a scanner. Monitor the displacements of the tip as a measure of tip-sample interaction forces. Record the movements at many tip-sample distances along vertical direction in a certain position by clicking on "force measurement" item.

4.1.2) Obtain force measurements using a AFM under atmospheric conditions from an RCA-cleaned Si substrate with 2-3nm layer of natural oxide as well as from a C_{84}-embedded Si substrate and a Si substrate coated with a thin film of SiC.

4.1.3) Using AFM software, plot Force-distance curves under atmospheric conditions. Note: The AFM cantilever was a Si probe with a tip radius of ~5–20 nm and spring constant of ~40 N/m.

4.2) Measure the stiffness of C_{84} embedded Si substrate in UHV chamber

4.2.1) Obtain force measurements according to the guidance of 4.1.1 using a AFM in a UHV system from an RCA-cleaned Si substrate, a clean Si(111)-7x7 surface, a C_{84}-embedded Si substrate, substrate and a Si substrate coated with a thin film of SiC.

4.2.2) Plot Force-distance curves in a UHV system. Note: The AFM cantilever was a Si probe with a tip radius of ~5–20 nm and spring constant of ~40 N/m. Figure 4 presents the force-distance analysis of disordered Si surface, 7x7 surface, single self-assembled layer of C_{84} embedded within Si surface, and Si surface, as determined using UHV-AFM.

5. Measurement of nanomechanical properties by MD simulation

Note: In the simulation section, OVITO[16] (open-source visualization software) and, oSSD[17] (Open surface structure database) are used to create the simulation model and results visualization. LAMMPS[14] (an open-source molecular dynamics (MD) simulation package) is employed to perform the nanoindentation simulation and analyze the simulation results[15]. All the simulation jobs are performed with parallel computing in the Advanced Large-scale Parallel Supercluster (ALPS) of NCHC.

Note: To study the C_{84} monolayer/Si substrate heterojunction by using MD simulation, one should prepare a simulation model by several steps to obtain a relaxed C_{84} monolayer embedded into the Si substrate. Note that it is difficult to generate an exactly the same structure from the experimental data, because of the complex of the inter structure between C_{84} monolayer and Si (111) substrate heterojunction. As a result, we use an artificial way to generate the simulation model with several steps of procedure, which is illustrated in Figure 5. The details are described in the following protocols. We describe how to setup the parameter of MD in LAMMPS, establish a relaxed C_{84} fullerence monolayer embedded into a substrate, perform an indentation procedure, and analyze the simulation results.

5.1) Parameter setting in LAMMPS input file

5.1.1) Use boundary command to set the periodic boundary conditions in the x- and the y-directions.

5.1.2) Use “fix velocity” command to assign the initial velocity with a Gaussian distribution on each atom of the system, randomly.

5.1.3) Use “fix pair_style” command to assign Tersoff[18] and AIREBO[19] potentials to describe the Si-Si and Si-C interaction and the C-C interaction, respectively.

5.1.4) Use “fix nvt” and “fix npt” command to adopt the Nosè-Hoover method[20] to ensure the system remains at the desired temperature and pressure to generate a canonical and isothermal-isobaric ensemble[20], in which system the velocity-Verlet algorithm20 is employed to predict the trajectories of the atoms. Use both “fix nvt” and “run” commands to set a cooling rate of 3 K/ps for annealing process.

5.1.5) Use “timestep” command to set a time step of 0.2 fs as the time integration.

5.1.6) Use “fix wall/reflect” command to adopt a reflected wall to confine the degree of freedom. (5.3.2)

5.1.7) Use “region” and “group” to divide the substrate into different control layers (5.4.3): Newtonian atom layer, a thermal control layer, and a bottom fixed layer, which can be set up by using “fix nve”, “fix nvt”, and “fix setforce” commands, respectively.

5.1.8) Use “region” and “create_atoms” commands to create a spherical probe.

5.1.9) Use “fix move” command to embed the C84 monolayer into the substrate (5.4.2) and move the probe during the simulation. (5.5.2)

5.1.10) Use “run” command to perform MD simulation.

5.1.11) Use “compute force” (5.6.1) and “compute stress/atom”(5.6.4) commands to evaluate the atomic stress and indentation force.

Note: In the following, except the structure establishing, all the steps were done by LAMMPS script.

5.2) Use oSSD and OVITO to preparation of Silicon (111) 7x7 surface.

5.2.1) Turn on the oSSD software. Click on the “search” button. “Search criteria” panel is presented. Chose Si substrate, elemental type, reconstructed structure, semiconductor elec, diamond lattice, 111 face and 7x7 pattern. Click on the “Search” and “Accept” buttons. “Structure list” panel is presented. Click the desired structure (i.e.Si(111)-7x7). Click the “File” button. Save the coordination file as .xyz file.

Note: We point out that the structural database extracted from oSSD is not large enough for our indentation simulation. As a result, we rebuild a larger and thicker substrate by the following steps.

5.2.2) Turn on the OVITO software. Load the .xyz file into OVITO. Use “Slice” command to capture a supercell of the Si(111)7x7 surface with size of 26.878x46.554Å^2 in x and y direction. Export the data file. Use “Slice” command to capture a supercell of the bottom Si(111) substrate with size of 26.878x46.554x9.7 Å^3. Use “Show periodic images” command to duplicate the supercell 12 times in z direction. Export the data file.

5.2.3) Combine the data files of Si(111)7x7 surface and the Si(111) substrate models by Notepad++ (a free source code editor). Finally, load the combined data into OVITO. Use “Show periodic images” to duplicate a 5x3 supercell in x and y directions to enlarge the size of substrate.

5.2.4) Use LAMMPS to perform a 20 ps MD simulation time for relaxing the simulation model. In the following, perform a quench process from 1550 K to room temperature for 500ps simulation time. Finally, perform a 10 ps simulation time for the final relaxation process.

5.3) Preparation of C_{84} fullerence monolayer

5.3.1) Download the coordination file of the Optimized structure of C84 fullerene from the web[21] and write a FORTRAN program to replicate 49 C84 fullerenes arranged in a honeycomb structure.

5.3.2) Use LAMMPS to setup reflect walls upon and below the C_{84} monolayer to ensure that the molecules stay on a plan. Perform a MD simulation time for 200ps to relax the simulation model. In the following, perform a quench process from 700 K to room temperature to obtain a glob minimum state for 500ps simulation time. Finally, perform a 10 ps simulation time for final relaxation process.

5.4) Establish the indentation model of C_{84} fullerence monolayer on Silicon (111) 7x7 surface.

5.4.1) Write a FORTRAN code to lay the C_{84} monolayer on the Si(111)7x7 surface with distance of 3 Å to establish the indentation model.

5.4.2) Use LAMMPS to embed the C_{84} monolayer into the substrate with depth of 2~3 Å. In the following, run a 40ps simulation time for system relaxation. Finally, anneal the system to room temperature.

5.4.3) Divide the silicon substrate into a top Newtonian atom layer, a thermal control layer, and a bottom fixed layer, which are 0.7, 2, and 5.3 nm in thickness, respectively. The C_{84} monolayers were also modeled as a Newtonian atom.

5.5) Indentation Process of MD

5.5.1) Use LAMMPS to create a spherical probe with 5nm in diameter upon the C84/Si(111)7x7 surface mode.(Fig. 5) The probe is set as a rigid body. Specify a constant velocity of 10m/s on the probe to move downward toward the specimen in the indentation process.

5.5.2) Move the probe downward to the specimen at a constant speed until the specific loading depth (i.e. including the cases of 1.5, 2.5, 4.5, 10, 15, 20, and 30Å so as to explore the effect of the C84 fullerenes monolayer on the Si substrate, where the size of C84 fullerene is 11 Å) in the loading process. Hold the probe in the substrate in the holding process to allow for the relaxation of atoms. Finally, extract the probe from the substrate at a constant speed in the retraction process.

5.6) Calculation and analysis

5.6.1) Calculate the indentation force by summing the vertical force of atoms in the probe according to the following formulas:

$$F_Z = \sum_{i=1}^{N_{prob}} f_{i,z} \qquad \text{……. (1)}$$

5.6.2) Extracted the reduced modulus and stiffness from the force-distance curve of indentation. Based on Oliver and Pharr's method[22], a linear relation can be derived between the Young's modulus and the unloading stiffness. The stiffness (i.e., the slope of the initial portion) of the unloading curve is defined as

$$S = \frac{dP}{dh} = \beta \frac{2}{\sqrt{\pi}} \sqrt{A} E_r \qquad \text{……. (2)}$$

where P, h, A, and E_r are the indentation load, elastic displacement of probe, projected area of the indentation, and reduced modulus. β (=1 for circular indenter) is the shape modification factor. The relationship between reduced modulus and Young's modulus can be written as

$$\frac{1}{E_r} = \frac{(1-v^2)}{E} + \frac{(1-v_i^2)}{E_i} \qquad \text{……. (3)}$$

where E and *v* are the Young's modulus and Poisson's ratio for the specimen and E_i and v_i are the the Young's modulus and Poisson's ratio for the indenter.

5.6.3) Calculate the hardness by definition of $\mathrm{H} = P_{max}/A$, where P_{max} and A are the maximum indentation force and projected area of probe.

5.6.4) Calculate the virial atomic stress[22] on the *m* plane of the substrate in the *n*-direction by

$$\sigma_{mn} = \frac{1}{N_S}\sum_i \left[\frac{m_i v_i^m v_i^n}{V_i} - \frac{1}{2V_i}\sum_j \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \frac{x_{ij}^m x_{ij}^n}{r_{ij}} \right] \quad \text{……. (4)}$$

where m_i is the mass of atom *i*; v_i^m and v_i^n are the velocity components of atom *i* in the *m*- and *n*-directions, respectively; V_i is the volume assigned around atom *i*; N_s is the number of particles contained within region S, where S is defined as the region of atomic interaction; $\phi(r_{ij})$ is the potential function; r_{ij} is the distance between atoms *i* and *j*, and x_{ij}^m and x_{ij}^n are the *m*- and *n*-direction components of the vector from atom *i* to atom *j*.

5.6.5) Use OVITO to show the von-Mises strain of each atom invariant according to the following formulas:

$$\varepsilon^{Mises} = \sqrt{\varepsilon_{23}^2 + \varepsilon_{31}^2 + \varepsilon_{12}^2 + \frac{(\varepsilon_{22}-\varepsilon_{33})^2+(\varepsilon_{33}-\varepsilon_{11})^2+(\varepsilon_{11}-\varepsilon_{22})^2}{6}} \quad \text{……. (6)}$$

REPRESENTATIVE RESULTS:

A monolayer of C_{84} molecules on a disordered Si(111) surface was fabricated using a controlled self-assembly process in a UHV chamber. Figure 1 shows a series of topographic images measured by UHV-STM with various degrees of coverage: (a) 0.01ML, (b) 0.2ML, (c) 0.7ML, and (d) 0.9 ML. The electronic and optical properties of the C_{84} embedded Si substrate were also investigated using a variety of surface analysis techniques, such as STM and PL (Figure 2). The excellent material properties of the resulting samples demonstrate how nanotechnology can be used for the control of matter at the atomic- and nano-scales. The MFM and SQUID results in Figure 3 show the surface magnetism of C_{84} embedded substrate. Figure 4 presents the UHV-AFM results that refer to the nanomechanics of proposed substrate. Our experimental results demonstrate the potential of the C_{84} embedded silicon substrate as an alternative to semiconductor carbide in nanoelectronic devices for high-temperature, high-power, high-frequency applications as well as in magnetic and MEMS devices (in Figure 4).

In the simulation section, all the procedures are completed by using LAMMPS to perform the MD simulations. The mechanical properties (indentation force and contact stress) of the fullerene embedded substrate is calculated and shown in Figure 6. The von-Mises strain analysis of atoms at different time step are used to characterize the local deformation. The corresponding snapshots as a function of indentation depth can be seen in the inserts of Figure 6, which were calculated and visualized by OVITO. The results of indentation force as a function of indentation depth are used to calculate the hardness *H*(Figure 7(a)), reduced modulus E_r(Figure 7(b)), and loading stiffness *S* (Figure 8) of the C84 monolayer. The results can be compare with that determined by experiment and provides a more detail point of view to interpret the variation of the mechanical property.

FIGURE LEGENDS:

Figure 1: C_{84} Embedded Si substrate with different coverage. Series of STM topographic images (40x40 nm^2) showing C_{84} molecules adsorbed on Si(111) surface at

a negative sample bias of 2V, as measured by UHV-STM with various degrees of coverage: (a) 0.01ML, (b) 0.2ML, (c) 0.7ML, and (d) 0.9 ML.

Figure 2: Electronic properties measurements on C_{84} Embedded Si substrate. (a) I-V curves and differential derivative conductance (dI/dV) vs the voltage curve of a single self-assembled layer of C_{84}, as determined by UHV-STM; (b) Field emission current density vs electric field curve; (c) Corresponding F-N plot of surface with embedded C_{84}, as measured using a source-measure unit; (d) Photoluminescence spectrum of single self-assembled layer of C_{84}. Re-print with permission from (reference 12)

Figure 3: Surface magnetism on C_{84} Embedded Si substrate. (a) MFM image of Si Substrate embedded with C_{84}; (b) Magnetization loop plotted against external magnetic field

Figure 4: Nanomechanical investigation on C_{84} Embedded Si substrate. Force-distance analysis of disordered Si surface, 7x7 surface, single self-assembled layer of C_{84} embedded within Si surface, and Si surface, as determined using UHV-AFM. Re-print with permission from (reference 11)

Figure 5: Flow chart for establishing simulation model. The dramatic illustrate the setting in MD simulation from a single layer C84 and Si(111)7x7 surface to a C84 monolayer embed into Si(111)7x7 model. The detail procedures can be seen in the section 5 of protocol.

Figure 6: Indentation force and Contact stress analysis. Indentation force (black) and Contact stress (blue) of C_{84} as a function of indentation depth. Inserts show the corresponding snapshots, where the different color indicates the corresponding von Mises strain (ε_{vM}) of all atoms. To clear display the strain localization, only the atoms with ε_{vM}>0.08 are shown in the snapshot.

Figure 7: Hardness and reduced modulus analysis. (a)Hardness and (b)reduced modulus variation as a function of indentation depth for the C_{84} monolayer on Si surface.

Figure 8: Loading stiffness analysis. Loading stiffness as a function of distance determined by MD simulations compared with that by AFM experiments for C_{84}/Si. Modified from reference 16

DISCUSSION:

In this study, a novel annealing process which is very much temperature-dependent to make substrate surface pre-melting for nanoparticles half-embedding into substrate without destroying nanoparticle structures is provided to fabricate a self-assembled monolayer of C_{84} on a Si substrate (Figure 1). The improved process can be further suggested for preparing other nanoparticles embedded semiconductor substrates. The properties of a C_{84}-embedded Si substrate can be revealed in atomic scale using an UHV-SPM. The dI/dV curves corresponding to band gap measurements of proposed substrates are determined by UHV-STM (Figure 2). The field emission parameters, including field enhancement factor, turn-on electric field, and current density, are detected using a field emission spectrometer. The photoluminescence spectra, MFM and SQUID measurements reveal that the C_{84}-embedded Si substrate with UV light emissions and existence of ferromagnetism (Figure 3) is highly applicable in optoelectronic and dilute magnetic semiconductor (DMS) devices.

The adhesion strength corresponding to nanomechanical properties (i.e., stress) of the C_{84}-embedded Si substrates can be measured using AFM (Figure 4). Our results demonstrate that the hardness of the proposed C_{84}-embedded Si substrate is comparable to that of SiC and Si surfaces, making it applicable as an abrasive material for cutting tools as well as a film in MEMS devices.

In the simulation section, the von Mises strain (ε_{vM}) analysis is capable to detect the local deformation of atomic structure, which is very difficult to be observed in experiment. However, it is not possible to characterize the phase transformation. Here, we suggest some useful indices such as coordination number and HA index[23] to examine the phase transformation. In the setting of the indentation model, we have to point out that the size of the substrate in plan direction must be at least three times larger than diameter of the probe for eliminating the size effect and the boundary condition limitation, which would affect the dynamics and force flow of atoms. In addition, due to the time limit of MD simulation, to study the indentation process, the probe should exert the specimen with a very fast speed compared to that in experiment. We note that such a loading speed is too high to come out the long-time atomic diffusion and migration behavior, but it is still suitable to observe and describe the plastic deformation behavior and material properties under mechanical loading[24] because the results can be recognized as approximately quasi-static in nature[25].

An alternative way to resolve this limitation is to employ an accelerating MD method[26]. However, they requires heavy computational costs so that it is difficult to perform a simulation model as large as ours. Eventually, we point out that the results from our MD simulation is qualitatively in agreement with AFM indentation experiment (Figure 8). In addition, we verify that the hardness and reduced modulus of the C84 monolayer embedded into the Si surface are comparable with those of the Si substrate (Figure 7), which is corresponded to that observed in experiment as mention in 3rd paragraph.

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DISCLOSURES:
The authors have nothing to disclose.

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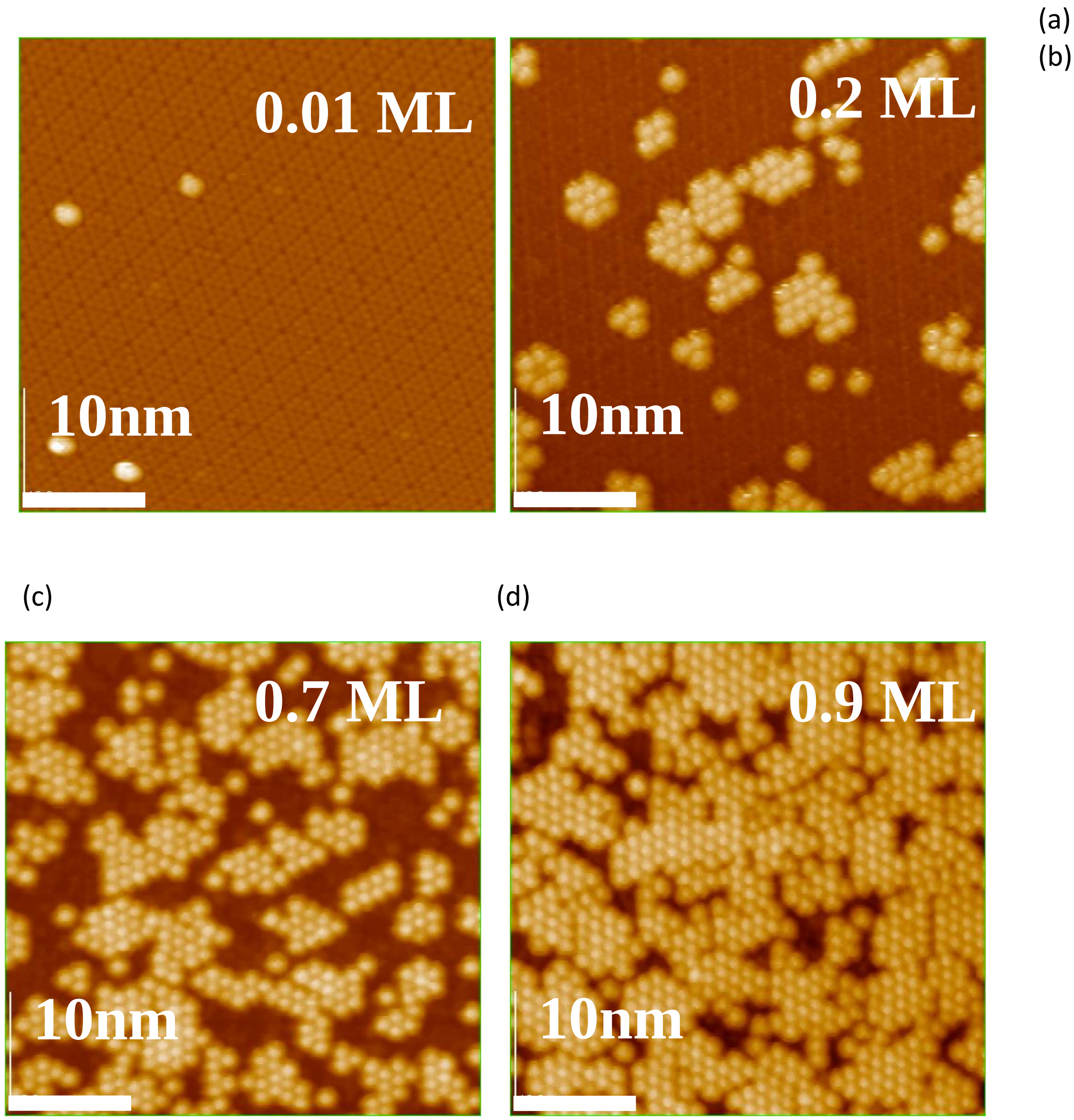

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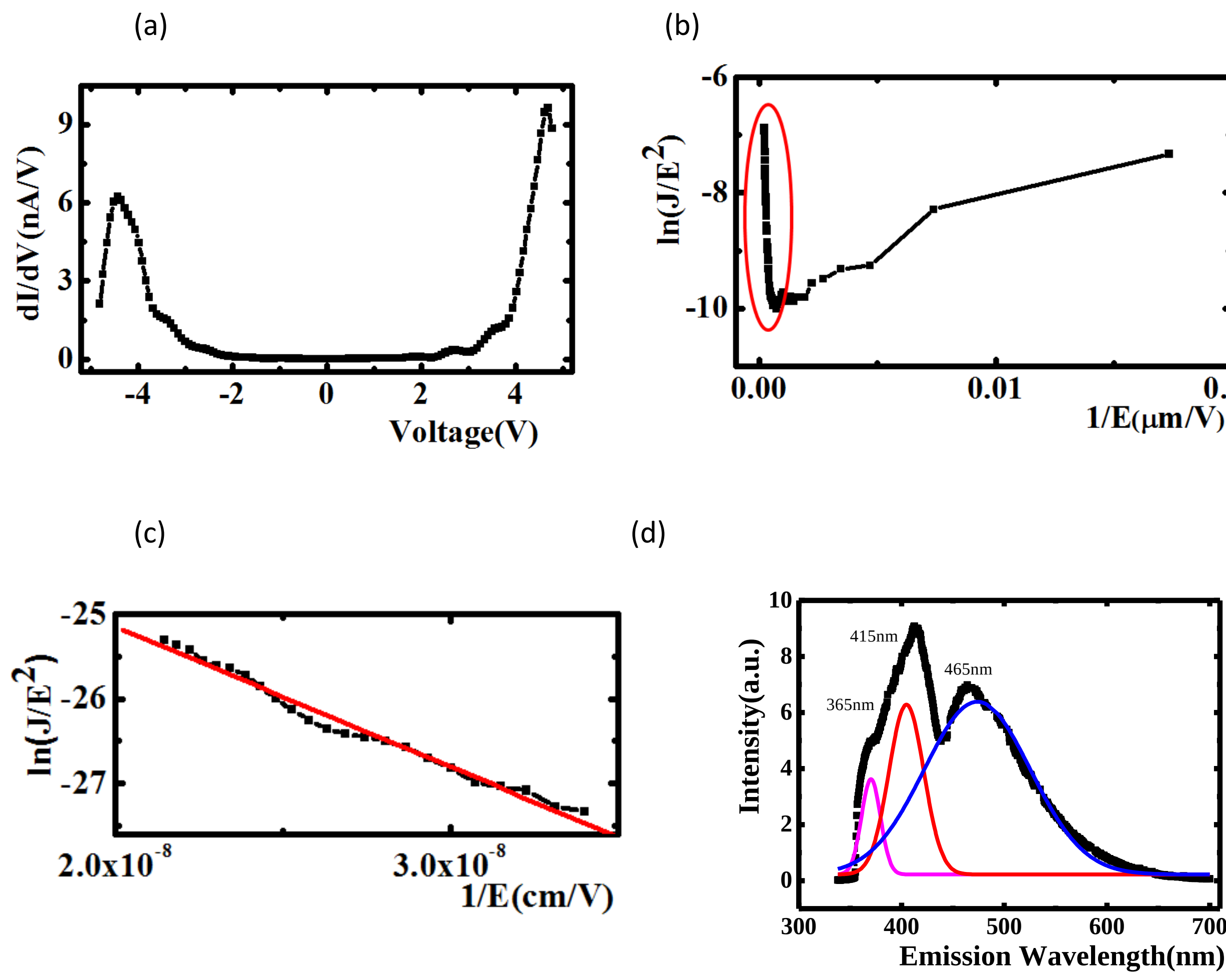
(a)
dI/dV(nA/V)
Voltage(V)
(b)
ln(J/E2)
1/E(μm/V)
(c)
ln(J/E2)
1/E(cm/V)
(d)
Intensity(a.u.)
Emission Wavelength(nm)
415nm
465nm
365nm

Figure 2

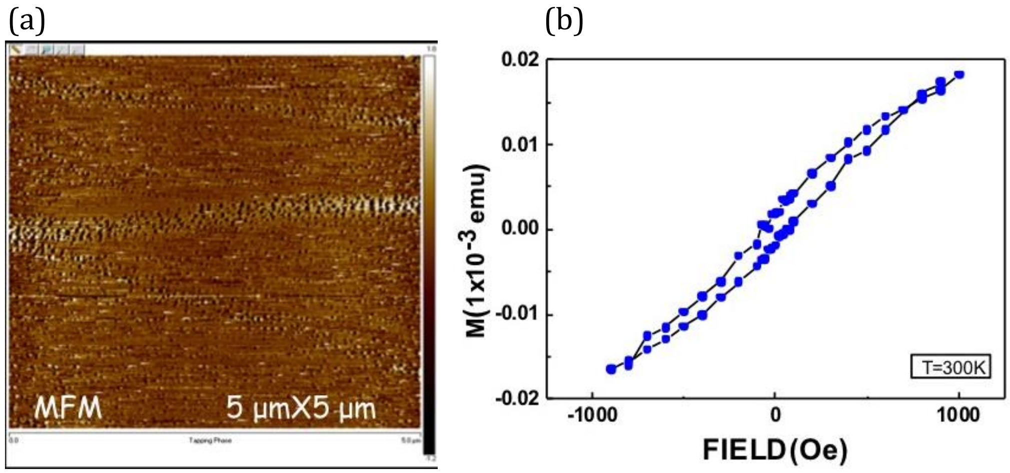
(a)
MFM
5 μmX5 μm
(b)
0.02
0.01
0.00
-0.01
-0.02
M(1x10-3 emu)
-1000
0
1000
FIELD(Oe)
T=300K

Figure 3

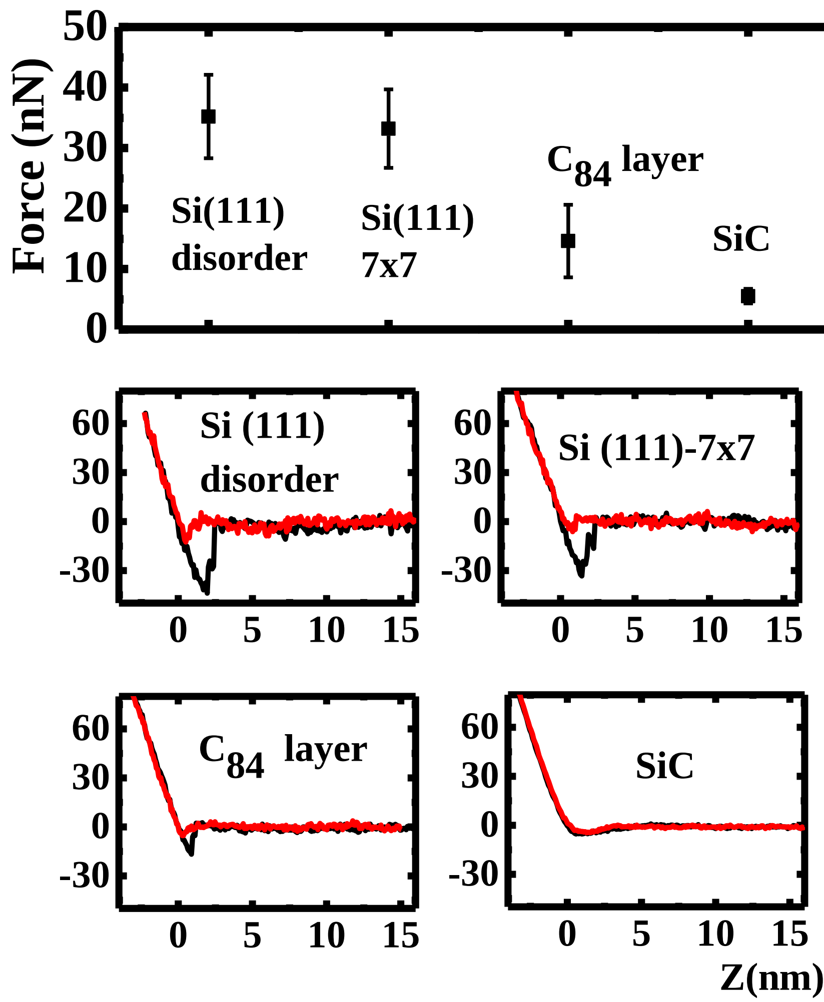
Force (nN)
50
40
30
20
10
0
Si(111) disorder
Si(111) 7x7
C84 layer
SiC
60
30
0
-30
Si (111) disorder
Si (111)-7x7
C84 layer
SiC
0
5
10
15
Z(nm)

Figure 4

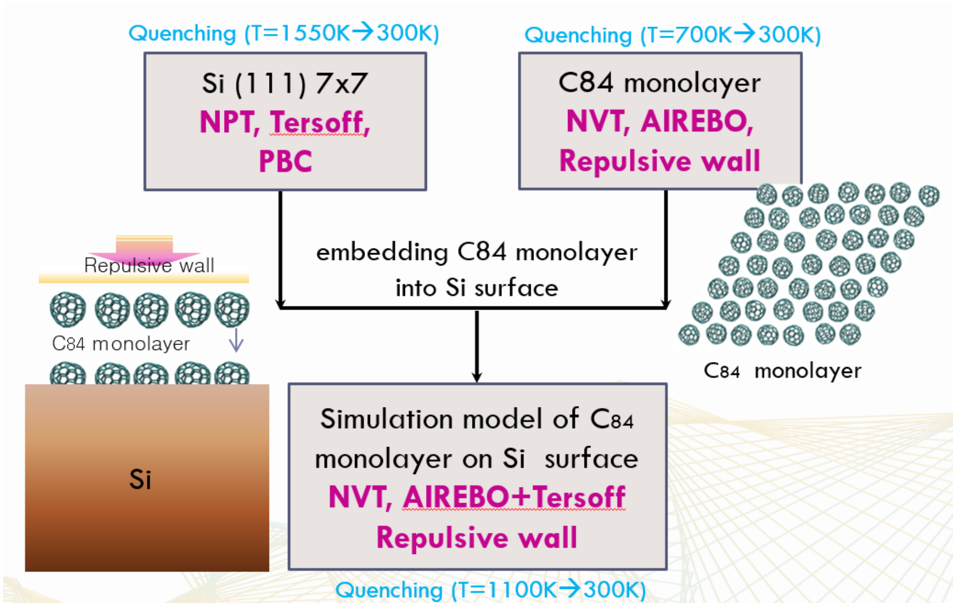

Figure 5

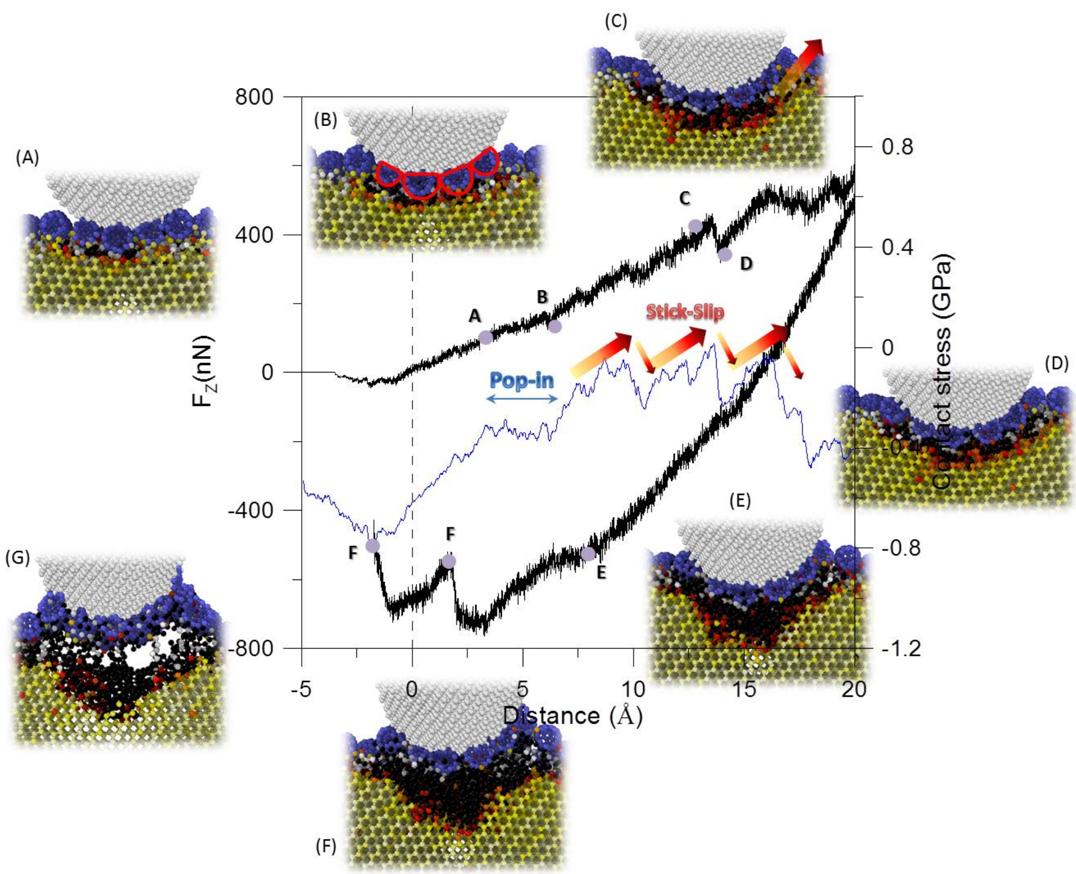

Figure 6

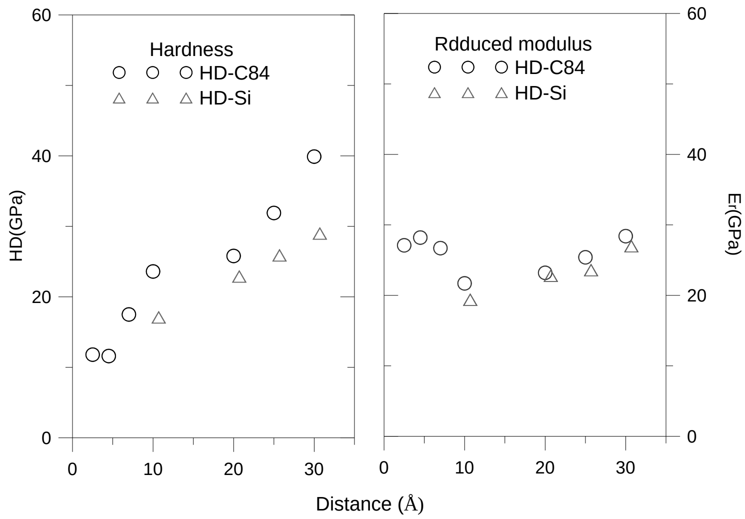

Figure 7

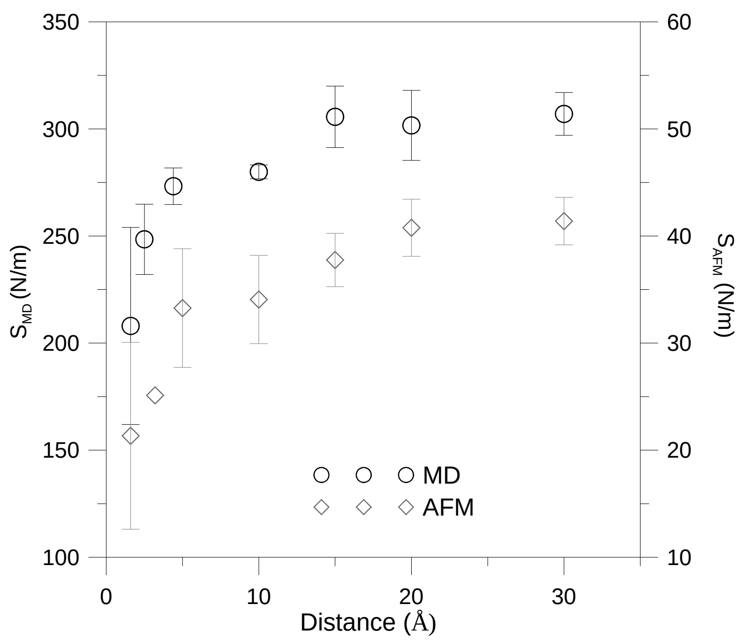

Figure 8

Name of Reagent/ Equipment	Company	Catalog Number
Silicon wafer		
Carbon,C_{84}	Legend Star	
Hydrochloric acid	Sigma-Aldrich	84422
Ammonium	Choneye Pure Chemical	
Hydrogen peroxide	Choneye Pure Chemical	
Nitrogen	Ni Ni Air	
Tungsten	Nilaco	461327
Sodium hydroxide	UCW	85765
Acetone	Marcon Fine Chemicals	99920
Methanol	Marcon Fine Chemicals	64837
UHV-SPM	JEOL Ltd	JSPM-4500A
Power supply	Keithley	237
SQUID	Quantum desigh	MPMS-7
ALPS	National Center for High-performance Computing, Taiwan	

Comments/Description

Si(111) Type/Dopant: P/Boron Resistivity: 0.05-0.1 Ohm.cm

C_{84} powder, 98%

RCA,37%

RCA,25%

RCA,35%

high-pressure bottle,95%

wire, diameter 0.3 mm, tip

etching Tungsten wire for tip,

suitable for liquid chromatography and UV-spectrophotometry

suitable for liquid chromatography and UV-spectrophotometry

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Response to the editor:

Thank you for your note and useful comments and suggestions on our manuscript. Enclosed please find a revised manuscript entitled "**Probing C84-embedded Si substrate using scanning probe microscopy and molecular dynamics**". We thank you for your careful review and insightful comments on our manuscript. We have revised the manuscript and would like to resubmit it. Below are the comments of the reviewer addressed point-by-point along with an attached revised manuscript. We have red-lined the significant changes in the revised manuscript for easier tracking. Please let us know if there is anything else that we can address with respect to this manuscript. Thank you for the consideration and we look forward to hearing your response.

Sincerely,

Editor's Comments to the Author

Authors have provided the stepwise instructions of software usage in section 5. We point out

Response to the Editor:

•There are several steps that will require additional detail in order to be filmed. These steps may be particularly difficult to visualize, given that they may involve manipulations in software. Because all of section 5 is computational, software manipulations must occur in a graphical user interface and stepwise detail regarding what is clicked on in the software must be provided.

-5.2.1/5.3.1/substeps of 5.4/5.5.1 – Please provide stepwise instructions of software usage in a graphical user interface. If this cannot be done, that is, scripting is involved, these steps should not be highlighted for filming. This applies to the entire section.

Response: Authors have provided the stepwise instructions of software usage in section 5. We point out that because the steps are too many, which would exceed the limitation of JoVE, the original highlight is canceled. We only highlight a paragraph in line 261-266.

•Protocol is discontinuous. Please highlight step 3.1.2 and 3.1.3 if 3.1.1 is to be filmed. 4.1.1 must be highlighted if 4.1.2 is to be filmed.

Response: Authors have highlighted step 3.1.2 and 3.1.3, and 4.1.1.

•Additional detail is required:

-1.3.1 – Which temperature is correct? 550 or 650?

Response: 650^0C is a better set-up. Authors have corrected the temperature to 650^0C.

-2.3.1- How is the system operated? Stepwise detail is required for filming.

Response: Authors have revised step 2.3.1 to make the process clear.

2.3.1) Place C_{84}-embedded Si substrate on a FE sample holder. Insert the holder into FE analysis chamber. Evacuate the chamber to a pressure of approximately 5 $\times 10^{-5}$ Pa for FE measurement.

-2.4.1 – How is the equipment operated for photon collection and analysis? Stepwise detail is required for filming.

Response: Spectrometer is a wisely used tool. We used the spectrometer to collect photons and measure the intensity of light as a function of wavelength.

Authors have revised the manuscript as:

"2.4.1) Transfer testing substrate to an optical emission measurement system. Focus a He–Cd laser source with 325 nm emissions on the substrate that is located in the center of the sample compartment. Set up a spectrometer in a suitable position. Use a spectrometer to acquire the photoluminescence spectrum by collecting and analyzing emitting photons. The optoelectronic result is shown in Figure 2(d).”

-3.1.2, 3.1.3 – Please provide stepwise detail regarding how these actions are achieved if this section is to be filmed. If software is used, please indicate what is clicked on in the graphical user interface.

Response: 3.1.2 and 3.1.3 have been revised as:

3.1.2) Place the magnetized sample on an MFM sample stage. Click on “Obtain MFM topography” item. Observe the microstructure of the fullerene in the magnetic domain embedded within the Si substrate using MFM in lift mode with the application of magnetization perpendicular to the surface of the sample.

3.1.3) Use a nano-scale PPP-MFMR cantilever for MFM measurements (Figure 3 (a)). Determine the surface magnetism if MFM topography appears darker(brighter) when the magnetic moment of tip is in the same(opposite) direction of the substrate moment.

-3.2.2 – How is the substrate magnetized?

Response: 3.2.2) Magnetize samples of C_{84}-embedded Si and C_{84} clusters on C_{84} embedded Si substrate prior to SQUID experiments by applying a magnet with a field strength of approximately 2 kOe.

-3.2.3 – How are the magnetization loops acquired? Stepwise detail regarding equipment use is required.

Response: SQUID system is an automatic measuring system. We place the sample into SQUID. Apply a sweeping magnetic field. Then we obtain the magnetization loops. The 3.2.3 has been revised as:

3.2.3) Place the sample in an SQUID. Apply a sweeping magnetic field in a range of ~ 2 kOe. Obtain the magnetization loops plotted versus the external magnetic field in SQUID measurements at room temperature.

-4.1.1 – A sharp what? How is the tip moved across the substrate? Please be more detailed regarding operation of the equipment so it is clear how measurements were made.

Response: Thanks for the comment. We have revised it as “a sharp tip”. Tip movement is controlled using a scanner. We have revised step 4.1.1 as:

4.1.1) Place the substrate on an AFM sample stage. Drag a sharp tip over the substrates using a scanner. Monitor the displacements of the tip as a measure of tip-sample interaction forces. Record the movements at many tip-sample distances along vertical direction in a certain position by clicking on “force measurement” item.

•Formatting

-2.1, 2.1.1 – Should FB be FE?

Response: Authors have made a correction.

-2.1.2 must be split into two steps.

Response: 2.1.2 has been split into 2.1.2 and 2.1.3. The previous 2.1.3 has been moved to 2.1.4.

-A space is required between 2.4.1 and 3.

Response: We have made a space.

-Please fix the step numbering throughout the protocol. There are many mistakes including two steps 3.2.2 and 5.3.2, and step 5.1.7 appears after step 4.2.2.

Response: The previous 3.2.2 and 5.3.2 has been revised to 3.2.3 and 5.3.3. 5.1.7 is canceled.

-Please check that that the text is consistent throughout the Materials/Equipment Table. In addition, please check that all items have been included in this table (e.g., vacuum system).

Response: We have checked the tables.

-Please ensure that spaces are included between steps (e.g., 5.2 and 5.2.1, etc.).

Response: Authors have included the space between 5.2 and 5.2.1.

-Please provide doi information for references where applicable, and abbreviate all journal titles.

Response: We have put the doi information for each reference.

•The manuscript must be copyedited for grammatical and typographical errors prior to acceptance. (Example: 2.2.1 – should be 'the following:')

Response: Authors have made a correction.

•Unnecessary branding should be removed from the Figure 2 legend - Keithley 237.

Response: "Keithley 237" has been removed.

•As written, the Discussion still focuses too heavily on the results, rather than the method. Please reformat this section to that it also emphasizes the future applications and advantages of this method over others.

Response: The discussion has been revised as:

In this study, a novel annealing process which is very much temperature-dependent to make substrate surface pre-melting for nanoparticles half-embedding into substrate without destroying nanoparticle structures is provided to fabricate a self-assembled monolayer of C_{84} on a Si substrate (Figure 1). The improved process can be further suggested for preparing other nanoparticles embedded semiconductor substrates. The properties of a C_{84}-embedded Si substrate can be revealed in atomic scale using an UHV-SPM. The dI/dV curves corresponding to band gap measurements of proposed substrates are determined by UHV-STM (Figure 2). The field emission parameters, including field enhancement factor, turn-on electric field, and current density, are detected using a field emission spectrometer. The photoluminescence spectra, MFM and SQUID measurements reveal that the C_{84}-embedded Si substrate with UV light emissions and existence of ferromagnetism (Figure 3) is highly applicable in optoelectronic and dilute magnetic semiconductor(DMS) devices. .

If your figures and tables are original and not published previously, please ignore this comment. For figures and tables that have been published before, please include phrases such as “Re-print with permission from (reference#)” or “Modified from..” etc. And please send a copy of the re-print permission for JoVE’s record keeping purposes.
JoVE reference format requires that DOIs are included, when available, for all references listed in the article. This is helpful for readers to locate the included references and obtain more information. Please note that often DOIs are not listed with PubMed abstracts and as such, may not be properly included when citing directly from PubMed. In these cases, please manually include DOIs in reference information.
Response: We have made doi links.

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

The submitted paper entitled "Probing C84-embedded Si substrate using scanning probe microscopy and molecular dynamics" reports a protocol for fabricating and measuring C84 arrays embedded Si substrate. The idea is interested and useful for the application of nanotechnology. The detail of both simulation and experiment skill are clearly described in the manuscript. I recommend this article to be published in JoVE after making the following revisions.

1.In protocol section (5.4.1 ~5.4.3 and 5.5.1), author should describe how do you make those procedure (by LAMMPS, OVITO, or programing,) in your simulation procedure.

Response: Authors have provided the stepwise instructions of software usage in section 5. We point out that because the steps are too many, which would exceed the limitation of JoVE, the original highlight is canceled. We only highlight a paragraph in line 261-266.

2.In representative result section (1st paragraph), what is the abbreviation "PL" mean in 1st paragraph.

Response: Thanks for the suggestion. Authors has corrected "PL" as "Photoluminescence(PL)" to make it clearly.

3.In discussion section: (1)In 1st paragraph, what is the novel annealing process mean? How does the novel method compare to the old method ? what does it improve ? (2)In 4th paragraph, authors suggest the HA and CN to characterize the phase transformation. Do those applied in this work to analyze the simulation results? What is its limitation?

Response: (1) The novel annealing process means we have to take many steps repeatedly (Step. 1 in Protocol) which are very much temperature-dependent to make substrate surface pre-melting for nanoparticles half-embedding into substrate without destroying nanoparticle structures. The traditional process either makes nanoparticle just lie on surface, or dissociate to form amorphous structures with substrate atoms.

(2) HA and CN are not applied in this work for analyzing the simulation results. CN is used to identify the number of the most neighbor atom. Instead, HA provides very clear information about the local symmetry of atomic arrangement more than the common pair correlation function and coordination number, and has been used to simulate the grain boundary microstructure transition, local cluster structure, and glass forming of metallic alloys under the rapid cooling condition. Both indexes can provide the quantitative difference between different phases.

4.In Figure 1, please check the format.

Response: Authors have converted the Fig.1 again in their manuscript.

5.In Figure 6, please indicate the which curve correspond to Fz, and which curve correspond to the contact stress. In addition, label G is not shown.

Response: Authors have indicated the corresponding curves in the figure legends.

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

N/A

Response: Thanks for the comments.

Reviewer #2:

Manuscript Summary:

This paper is an interesting manuscript,it gives an array-designed C84-embedded Si substrate fabricated method. The properties of the samples were measured by many kinds of technologies. On the other hand, the measured parameters were explained by Molecular dynamics (MD) siulations. Their results should be beneficial to the community interested in fabrication of FED,optoelectronical device, MEMS cutting tools. The fabricated and simulation method are technically correct.

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

N/A

Response: Thanks for the comments.

Reviewer #3:

Manuscript Summary:

The authors reported on an array-designed C84-embedded Si substrate fabricated using a controlled self-assembly method in an ultra-high vacuum chamber. The characteristics of the C84-embedded Si surface, such as atomic resolution topography, local electronic density of states, band gap energy, field emission properties, nanomechanical stiffness, and surface magnetism, were examined using a variety of surface analysis techniques under UHV conditions as well as in an atmospheric system. The experimental findings have been duly supported through the relevant discussions.

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

N/A

Response: Thanks for the comments.

Reviewer #4:

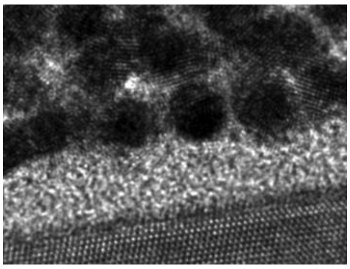
Manuscript Summary:

This article introduces the method of fabricating the material of C84 embedded Si substrate. The authors exploit different techniques, such as STM, field emission, photoluminescence, MFM, AFM, and SQUID to characterize the properties of this material. It turns out that C84 embedded Si substrate has wide band gap energy, high field emission current density, UV and near UV light emission, ferromagnetic property, and hardness comparable to that SiC and Si surfaces. Because of these properties, the authors expect that the material of C84 embedded Si substrate is possible to replace SiC, and has potential applications on field emission display, optoelectronic device fabrication, MEMS cutting tools.

Major Concerns:

1. It would be better if the authors demonstrate the evidence that C84 is embedded in Si substrate in Fig. 1 because it is an important point in this article. The current Fig. 1 just shows C84 on Si substrate.

Response: We thank reviewers for their very important comments. According to the instruction of JoVE, the editors suggested us to present detailed method, data analysis with certain technologies. The processes of experiments are the key issues in this article. The research results are not the major concerns in JoVE papers. Still we attach one TEM figure here for review's reference. The cross-section SPM results along with TEM images indicated C84 embedment will soon publish in other journal.



- A cross section TEM image of C84 embedded Si substrate

2. In 2.2.1), the authors state that I-V curves were obtained on Si(111)-7x7 surface, single individual C84 nanoparticles on Si, 7-19 C84 clusters on Si, 20-50 C84 clusters on Si, and a monolayer of C84 embedded within Si surface. However, in Fig. 2(a), only spectrum of single self-assembled layer of C84 is shown. I suggest the authors to show all of spectra in Fig. 2(a) for comparison.

Response: We thank reviewers for their comments. The editor office suggested us remove detailed results from previous version due to the policies and focuses of JoVE. We attached the figure here for review's reference. The figure has been published in ***RSC Adv.***, 3 (24), 9234 – 9239 (2013).

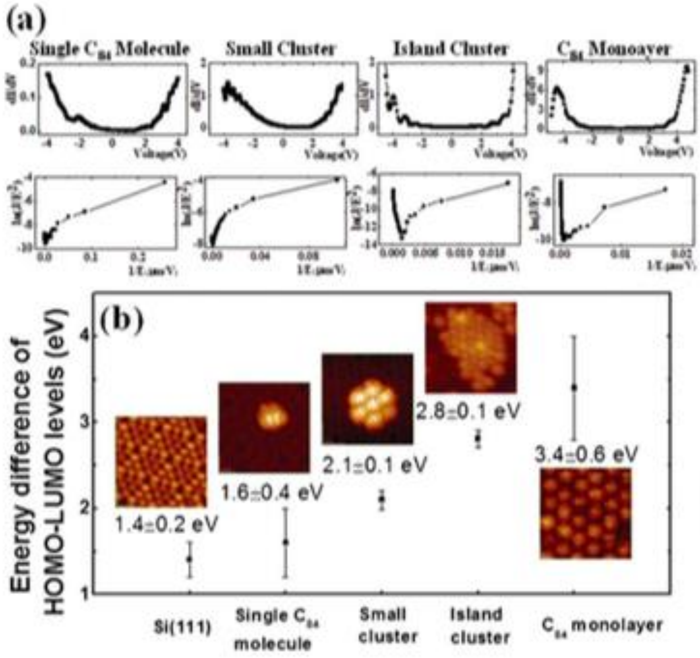


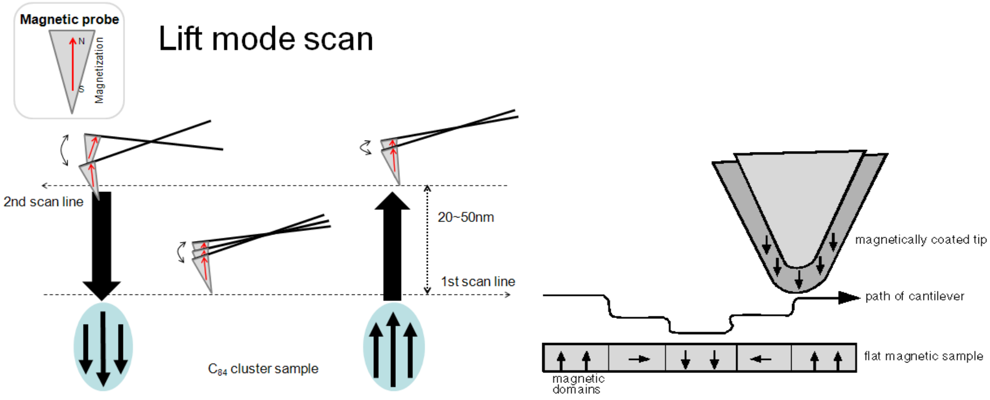
Fig. 5 (a) Current *versus* voltage curves and corresponding F–N plots for single C_{84} molecules, small-clusters, island-clusters and a single layer of self-assembled C_{84} substrate, determined by UHV-STM. (b) The energy difference between the HOMO and LUMO levels of the Si surface for clean 7 × 7 surfaces, single C_{84} molecules, small-clusters, island-clusters and a single layer of self-assembled C_{84}.

3. It is surprised that C84 embedded in Si reveals ferromagnetic property. However, the authors have no elucidation for this interesting finding. It would be better if the authors interpret why the contrast in MFM image in Fig. 3(a) can reflect the surface has the ferromagnetic property. In 3.2.2), the authors state that SQUID measurements were performed at room temperature and 5 K. However, in Fig. 3(b), only the loop at room temperature is shown. I suggest the authors to show the loop at 5K as well for comparison.

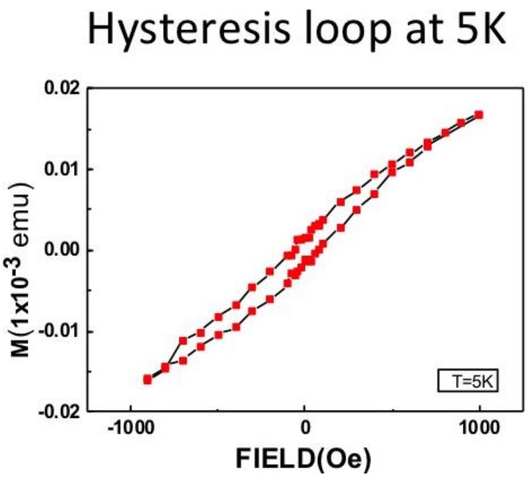
Response: We really thank for reviewer's comments. The reviewer pointed out the very important issue in this research. However, in this manuscript we only focus on the protocol of fabricating C84 embedded Si substrate due to the journal policies. The detailed mechanism revealing surface ferromagnetism will be published soon in other journal paper.

The operating principle of MFM is the same as in AFM, but with lift mode scanning. If substrate surface has no ferromagnetism, the MFM image looks like a flat surface without any signal. If substrate surface has ferromagnetism, the MFM topography would appear darker(brighter) when the magnetic moment of tip is in the same(opposite) direction of the substrate moment. We revised the 3.1.3) as following:

3.1.3) Use a nano-scale PPP-MFMR cantilever for MFM measurements (Figure 3 (a)). Determine the surface magnetism if MFM topography appears darker(brighter) when the magnetic moment of tip is in the same(opposite) direction of the substrate moment.



There is only limited space for presenting results. We removed the 5K description in our manuscript, but attached the SQUID result taken at 5K for reviewer's reference. The figure will be published soon in other journal paper.



Minor Concerns:

1. Line 19: should be "Center" instead of "Carter"

Response: Authors have made a correction.

2. Line 30: should be "Center" instead of "Carter"

Response: Authors have made a correction.

3. Line 36: should be "Center" instead of "Carter"

Response: Authors have made a correction.

4. Line 164: should be "LUMO" instead of "LOMO"

Response: Authors have made a correction.

5. Line 167: should be "FE" instead of "FB"

Response: Authors have made a correction.

6. Line 169: should be "FE" instead of "FB"

Response: Authors have made a correction.

Reviewer #5:

Manuscript Summary:

The authors have revised the manuscript as Reviewers' comments. Therefore, it can be published as it.

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

N/A

Response: Thanks for the comments.