Slutrapport

En ny typ av vit ljusemitterande diod med grafenkvantprickar

Energimyndighetens titel på projektet – engelska
A new type of white light-emitting diode using graphene quantum dots

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Nyckelord
Graphene, LED, Quantum dots

Förord

The rapid advancement of nanotechnology has opened new frontiers in the development of high-performance optoelectronic devices. Among these, graphene quantum dots (GQDs) have garnered significant interest due to their unique optical and electronic properties [1,2]. This report presents our efforts to develop a novel type of light-emitting diode (LED) utilizing GQDs grown on silicon carbide (SiC) pillars. Our research sought to optimize the growth conditions for graphene in designated regions, fabricate nanopatterned substrates, and characterize the resulting structures to evaluate their potential for optoelectronic applications. This project involved several intricate fabrication and characterization steps, including electron beam lithography, Raman spectroscopy, and hydrogen etching. Throughout the study, we encountered and addressed numerous challenges, such as achieving controlled graphene growth on the pillar tops and optimizing pillar spacing for enhanced device performance. Despite unforeseen delays, including those caused by the COVID-19 pandemic, we successfully demonstrated the feasibility of nano-sized graphene layer formation on SiC pillars, paving the way for further explorations in this field.

Innehållsförteckning

Sammanfattning

etta projekt syftade till att utveckla en ny typ av LED med grafen-kvantprickar (GQDs) odlade på pelare av kiselkarbid (SiC). Inledningsvis tillverkades SiC-substrat med mönstrade pelare i varierande storlekar med hjälp av elektronstråle-litografi och aluminium-masker. Tidiga försök att odla grafen resulterade dock i ett alltför tjockt lager. Genom att förfina processen lyckades man framställa nanoskaliga monoskiktsgrafen på pelartopparna, vilket bekräftades genom reflektanskartläggning och Raman-spektroskopi.Försök att minska avståndet mellan pelarna till under 50 nm försvårades av tillverkningsutmaningar, men en separation på 500 nm uppnåddes med pelare som var 400 nm breda och 500 nm höga. Raman-analyser bekräftade bildandet av grafennanostrukturer på dessa ytor. För att övervinna begränsningarna med e-stråle-litografi var väteetsning mycket användbar, vilket reducerade pelardiametern till cirka 60 nm, även om problem kvarstod med de stora hexagonala baserna.Fotoluminescens (PL)-mätningar var framgångsrika för pelare med en diameter på 1 µm men ineffektiva för mindre storlekar. Vissa prover dopades med grafen för vidare studier. Parallellt undersöktes i teoretiskt arbete, med hjälp av densitetsfunktionalteori (DFT), hur storlek och form på grafen-nanoflingor påverkar de optiska egenskaperna, vilket visade att spektrala egenskaper kunde justeras.Trots förseningar på grund av COVID-19-relaterade störningar förbereder teamet nu ett manuskript för publikation och söker ytterligare finansiering för att fortsätta forskningen.

Summary

This project aimed to develop a novel LED using graphene quantum dots (GQDs) grown on silicon carbide (SiC) pillars. Initially, SiC substrates with patterned pillars of varying sizes were fabricated using electron beam lithography (EBL) and aluminum masks. However, early graphene growth attempts resulted in excessive thickness. Refining the process led to the successful formation of nanoscale monolayer graphene on the pillar tops, as confirmed by reflectance mapping and Raman spectroscopy. Efforts to decrease the spacing between pillars to below 50 nm were hindered by fabrication challenges, but a 500 nm spacing with 400 nm-wide, 500 nm-tall pillars were achieved. Raman analysis confirmed graphene nanostructure formation on these surfaces. To overcome the limitations of e-beam lithography, hydrogen etching was very useful, reducing pillar diameters to approximately 60 nm, though issues remained with the large hexagonal bases of the pillars. Photoluminescence (PL) measurements were successful for 1 µm-diameter pillars but ineffective for smaller ones. Some samples were doped with graphene for further study. Parallel theoretical work using density functional theory (DFT) investigated the influence of graphene nanoflake size and shape on optical properties, revealing tunable spectral features. Despite COVID-19-related disruptions delaying some objectives, the team is preparing a manuscript for publication and seeking additional funding to continue the research.

Inledning/bakgrund

Conventional LEDs rely on phosphor-coated blue LEDs to generate white light, but this approach suffers from long-term color degradation, low color rendering index (CRI), and reliance on costly rare earth metals [3]. As a solution, this project aims to develop a rare-earth-free graphene quantum dot LED (GQD-LED) using silicon carbide (SiC) and graphene, offering a stable, eco-friendly alternative. Graphene quantum dots (GQDs) have demonstrated superior optical properties compared to traditional semiconductor quantum dots, including tunable luminescence through size and doping modifications. By leveraging our expertise in epitaxial graphene growth and optical tuning [4], we planned to explore how doping influences GQD photoluminescence, potentially enhancing their applicability in energy-efficient lighting. The fabrication of GQDs typically involves either top-down or bottom-up synthesis methods, but existing approaches face challenges such as high costs, limited control over optical properties, and low production efficiency. This project introduces a novel synthesis method that combines top-down and bottom-up approaches through sublimation growth on pre-patterned SiC substrates. By exploiting the distinct growth behaviors on polar and non-polar surfaces, we can engineer high-quality GQD arrays with controlled optical properties. Our previous studies indicate that monolayer graphene can be selectively grown on the top surfaces of SiC nanostructures, while computational modeling suggests that strain effects influence graphene’s electronic activity. Through careful optimization of growth conditions and buffer layers, this project aimed to achieve large-area, uniform GQDs with tailored emission properties, paving the way for high-performance optoelectronic applications.

Genomförande

The implementation of this project involved a systematic approach to fabricate and optimize GQDs on SiC pillars. We began by patterning SiC (0001) substrates using electron beam lithography with aluminum masks to create two sizes of cone frustums featuring flattened top surfaces of approximately 1 µm in diameter with 1 µm heights. After successful growth of monolayer graphene (using sublimation method) on the top of this size of pillars, to enhance the LED design, we further experimented with reducing the inter-pillar spacing—despite difficulties in maintaining the pillar height below 500 nm. We successfully fabricated nanopillars with a 500 nm spacing, a 400 nm top diameter, and 500 nm height (Fig. 1 left). We also explored hydrogen etching (in a CVD reactor) as an alternative to e-beam lithography to further decrease the pillar diameter from 1 µm to about 60 nm (Fig. 1 right), although this introduced new challenges with the pillar bases.

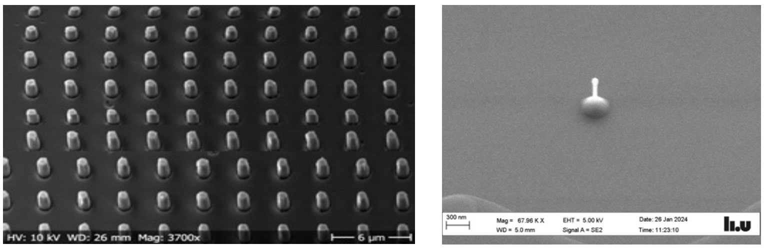

Fig. 1- *Left) Fabricated SiC pillars using EBL, Right) after* hydrogen etching

Resultat

Our results demonstrate the successful fabrication of graphene nanostructures on SiC pillars, marking a significant step toward the development of novel GQD-LEDs. Initial experiments using e-beam lithography yielded a thick graphene layer; however, after refining the growth conditions, we achieved nano-sized, monolayer graphene confined to the tops of the SiC pillars, as confirmed by both reflectance mapping (Fig. 2) and Raman spectroscopy showing clear G and 2D peaks (Fig. 3).

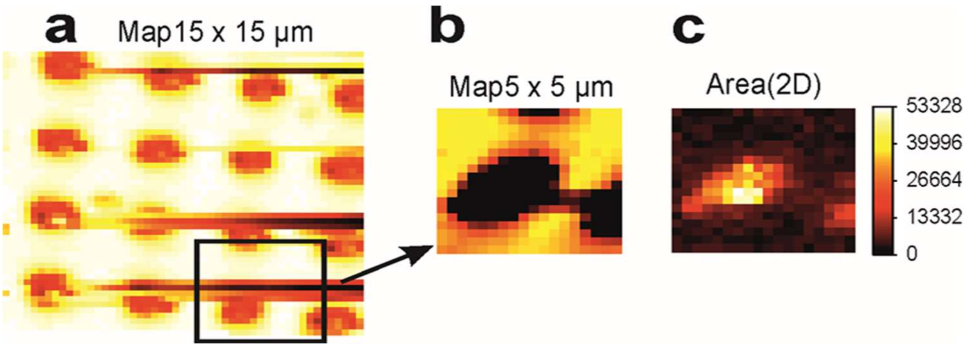

Fig. 2- *a) and b) Reflectance map of SiC pillars, c) Raman map of the same pillar in b.*

Furthermore, by incrementally reducing the inter-pillar spacing, we fabricated nanopillars with a 500 nm spacing and a 400 nm top diameter, and hydrogen etching further reduced pillar diameters to approximately 60 nm, despite challenges posed by the pillar bases. Although photoluminescence measurements were effective for larger pillars, they were unsuccessful for smaller pillars. Our theoretical work demonstrates that flake shape and edge structure are critical to the optical spectra, and that peak positions can be tuned by adjusting flake sizes.

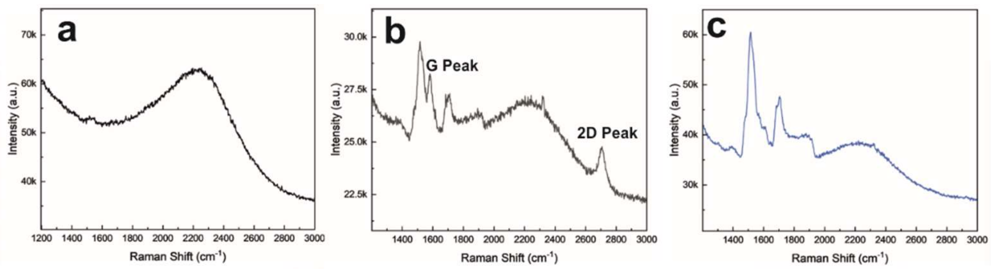

Fig. 3- *Raman spectra of SiC pillars sample* ***a)*** *before growth of graphene,* ***b)*** *after growth of graphene , c) Raman spectra of the same sample taken outside the SiC pillar region*

Unfortunately, the COVID-19 pandemic, which coincided with the start of our project, significantly disrupted lab work and contributed to delays, preventing us from achieving all project objectives. We plan to apply for additional funding to continue this research and address the remaining aims.

Diskussion

The results of this study demonstrate the feasibility of selectively growing nano-sized, monolayer graphene on the tops of SiC pillars, which marks a significant advancement in the development of graphene quantum dot (GQD) LEDs. Our approach, utilizing both e-beam lithography and hydrogen etching, successfully controlled the graphene layer thickness and confined its growth to the desired areas. This level of precision, as confirmed by Raman spectroscopy and reflectance mapping, not only highlights the potential for producing high-quality, monolayer graphene nanostructures but also underscores the advantages of integrating top-down and alternative fabrication methods. These findings are particularly important given the limitations of conventional phosphor-based LED technologies and the increasing demand for environmentally friendly and cost-effective lighting solutions.Despite these promising outcomes, several challenges remain that must be addressed to fully realize the potential of GQD-LEDs. The difficulties encountered in reducing the inter-pillar spacing below 500 nm and the issues with photoluminescence measurements for smaller pillars indicate that further optimization of the fabrication process is necessary. Additionally, the incomplete characterization of doped samples suggests that more work is required to understand the influence of doping on the optical and electronic properties of these graphene nanostructures. Future research will focus on refining these fabrication techniques and exploring the effects of additional doping elements, with the goal of achieving consistent, high-performance LED devices.

Publikationslista

Despite the above challenges, we are preparing a manuscript based on our experimental findings for journal publication.
Our theoretical work, published in Phys. Chem. Chem. Phys. 22 (2020) 8212 (Acknowledged the project), utilized density functional theory and its time-dependent version to analyze how the size and shape of graphene nanoflakes influence their magnetic structures and optical properties. These studies demonstrate that flake shape and edge structure are critical to the optical spectra, and that peak positions can be tuned by adjusting flake sizes.

Referenser, källor

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Bilagor