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Fourier-transform infrared spectroscopy of alkanethiol self-assembled monolayers formed on digitally photocorroded surfaces of (001) GaAs

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The science and technology of alkanethiol self-assembled monolayers (SAMs) on gold and other solid surfaces is a subject of ongoing research driven by the fundamental interest and attractive practical applications. The structural organization of alkanethiol SAMs is dominated by the strong intermolecular interaction, manifested by the enhanced quality of SAMs formed by long chain alkanethiols. Thiol ligands cover a larger number of binding sites on nanostructured rather than atomically flat gold surfaces,^{1,2} ascribed to the presence of curved surfaces of nanoparticles and vertices of nanostructured surfaces. The observation of this effect on surfaces of compound semiconductors, such as GaAs, is highly challenging due to the problem with maintaining surface stoichiometry and controlling oxide formation on these materials. Thus, there is anecdotal evidence that formation of high-quality SAMs on compound semiconductors requires flat surfaces.

We have investigated formation of mercaptohexadecanoic (MHDA) SAMs on digitally photocorroded (DIP) surfaces of (001) GaAs/Al_{0.35}Ga_{0.65}As nanoheterostructures (5 pairs of GaAs/AlGaAs, $d_{GaAs} = 12$ nm, $d_{AlGaAs} = 10$ nm). The DIP process allows etching with a step resolution of better than 0.1 nm, making possible also *in situ* deposition of different SAMs on freshly etched surfaces. The FTIR spectroscopy revealed the growing absorbance intensity and decreasing vibration energy of the -CH₂ modes of MHDA SAMs formed on surfaces of GaAs with the increasing nano-scale roughness produced in an ammonia solution. The absorbance amplitude of 1.08×10^{-2} ($E_{CH_2} = 2919.6$ cm⁻¹, FWHM = 20.3 cm⁻¹) observed for the SAM developed on the surface of the 5th GaAs layer was 11-fold greater than that on the surface of the 1st GaAs layer ($E_{CH_2} = 2922.0$ cm⁻¹, FWHM = 25 cm⁻¹), which suggests formation of an excellent quality MHDA SAM. Our results suggest the feasibility of attractive applications of the DIP process for the research of atomic scale interfaces involving III-V semiconductors and manufacturing of advanced sensors and nanodevices.

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