

Formation dynamics of hexadecanethiol self-assembled monolayers on (001) GaAs observed with photoluminescence and Fourier transform infrared spectroscopies

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Functionalization of the (001) GaAs surface with long-chain alkanethiol self-assembled monolayers (SAMs) has been investigated by several researchers [1-6]. However, relatively little is known regarding the mechanisms and kinetics of SAM formation on this substrate. Sample preparation is typically performed in an ethanolic thiol solution, with results reported for incubation times up to 26 hours. Formation dependence on incubation time has previously been studied using infrared absorption spectroscopy [5]. In addition, reports of post SAM formation photoluminescence (PL) increases have been made, demonstrating the net effect of GaAs surface passivation [4], presumably by the reduction of surface non-radiative recombination centers. Here, we report on the implementation of PL measurements for the observation of SAM process dynamics *in-situ*. Undoped epitaxial (001) GaAs prepared with hexadecanethiol (HDT) [HS(CH₂)₁₅CH₃] SAMs were used to record the PL effects of thiol chemisorption and SAM coordination over a 24 hour period. Comparing the time evolution of the PL signal with that of the bare GaAs surface, similarly exposed to the ethanol solvent, allowed us to observe the net increase and saturation of the PL intensity. Time-commensurate changes in both the absorption wavelength and intensity of the C-H stretching mode vibrations were measured using transmission Fourier-transform-infrared (FTIR) spectroscopy. We observed a double exponential increase of the time-dependent PL intensity, whereas the FTIR absorbance was approximated with a single exponential only. These findings are discussed in terms of the formation dynamics and the influence of the solvent properties on the thiolation process, particularly as may relate to recent studies concerning the bond strength and surface coverage of the SAM [7,8].

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