Surface Polymerization

GaAs–Polymer Hybrids Formed by Surface-Initiated Atom-Transfer Radical Polymerization of Methyl Methacrylate

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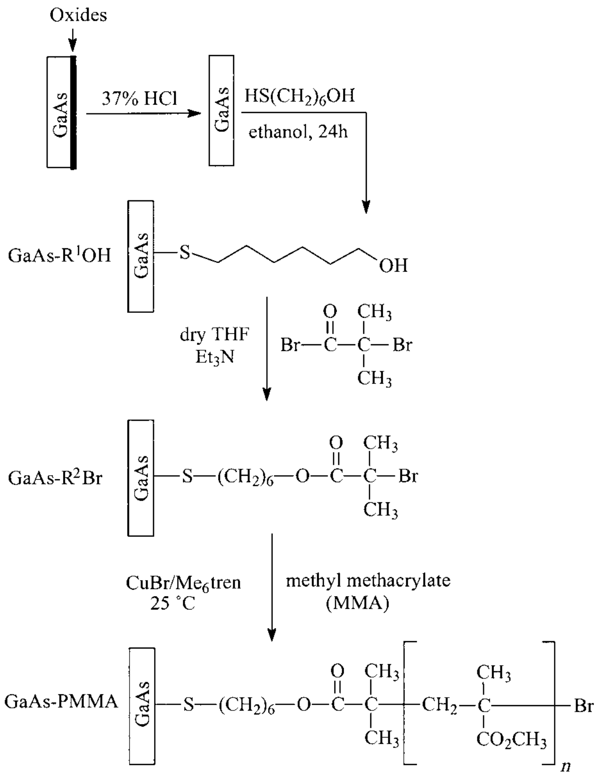
Semiconductor–polymer hybrids prepared by incorporating polymer brushes on semiconductor substrates have attracted considerable attention in recent years. The hybrids have unique surface and interface properties,[1–10] and allow the fabrication of nanopatterns.[11–16] Popular strategies for incorporating polymer brushes on substrates include the "top-down" or "grafting-to" approach, in which macromolecules are tethered directly onto the surface of a substrate, and the "bottom-up" or "grafting-from" approach, which attempts to grow polymer brushes from initiators anchored on a substrate surface. The latter approach can result in more densely packed polymer brushes.[17] Ionic (anionic[18–20] and cationic[6,21]), ring-opening,[11,22–26] radical,[17,27,28] nitroxide-mediated radical,[1] and atom-transfer radical[3–6,29,30] polymerizations have been used for surface graft polymerizations. Among these techniques, atom-transfer radical polymerization (ATRP) allows the preparation of well-defined polymers and polymer architectures, and exhibits good tolerance for functional groups and stability against impurities.[5,6]

Semiconductor–polymer hybrids prepared by surface-initiated polymerization on silicon substrates,[1–7] carbon nanotubes,[8–10] and germanium nanoparticles[31] have been reported. GaAs–polymer hybrids with well-ordered polymer brushes have potential applications in advanced GaAs-based semiconductor devices,[32] chemical sensors,[33] and biomaterials.[34] Recent developments in the preparation of Au–polymer hybrids by surface-initiated ATRP[16,35,36] and GaAs–organic hybrids from self-assembled monolayers (SAMs) of alkane thiols on GaAs[37] have inspired us to synthesize GaAs–polymer hybrids by ATRP. We also hoped that a dense, well-defined, and covalently bonded polymer nanofilm would help to stabilize the surface states[37,38] associated with this compound semiconductor.

We prepared GaAs–polymer hybrids by surface-initiated ATRP of methyl methacrylate (MMA) from ATRP initiators covalently immobilized on the (100)-oriented GaAs single-crystal surfaces. This process allows the preparation of GaAs–polymer hybrids with well-defined, covalently tethered polymer brushes. The strategy for preparing GaAs–polymer hybrids by ATRP is show in Scheme 1. A nearly stoichiometrically pure GaAs surface with reactive sites (dangling



Scheme 1. Covalent immobilization of ATRP initiators on the GaAs surface and surface-initiated ATRP to form the GaAs-PMMA hybrids.

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bonds) was obtained after the oxides on a 3 cm^2 GaAs(100) wafer were removed by treatment with concentrated HCl (37 %) for two minutes.[38] The GaAs substrate was subsequently immersed in a 5 mM ethanol solution of 6-sulfanyl-1-hexanol (which had been subjected to three freeze–pump–thaw cycles) for 24 h at room temperature to form the hydroxy-terminated GaAs surface (GaAs-R^{1}OH). The GaAs surface with immobilized ATRP initiators (GaAs-R^{2}Br) was obtained by immersing the GaAs-R^{1}OH substrate in a 0.1M THF solution of 2-bromoisobutyryl bromide containing 0.1M triethylamine for two minutes under argon. GaAs–polymer hybrids were finally prepared by surface-initiated ATRP of MMA on the GaAs-R^{2}Br surface in a continuously stirred solution containing 5.3 mL of MMA, CuBr (14.3 mg, 0.1 mmol), CuBr$_2$ (2.2 mg, 0.01 mmol), and tris[2-(dimethylamino)ethyl]amine[39] (Me$_6$tren, 26 µl, 0.11 mmol), for between 4 and 21 h at room temperature under argon.

Figure 1 a shows the As 3d and Ga 3d core-level spectra of the (100)-oriented GaAs single-crystal surface after HCl etching, as measured by X-ray photoelectron spectroscopy (XPS). The As 3d core-level spectrum shows a spin-orbit-split doublet, with binding energies (BEs) at about 40.7 eV ($3d_{5/2}$) and 41.4 eV ($3d_{3/2}$), attributable to the Ga*As* species.[40] The Ga 3d core-level spectrum has a peak component at a BE of about 19.0 eV associated with the GaAs species.[40] The As and Ga oxide species are absent in both spectra, thereby indicating that they have been completely removed by the treatment with concentrated HCl (Supporting Information).

Figure 1 b shows the As 3d and Ga 3d core-level spectra of the GaAs-R^{1}OH surface. The presence of As−S (BEs of about 42.0 eV ($3d_{5/2}$) and 42.7 eV($3d_{3/2}$)) and Ga−S (BE of about 19.7 eV) species on the GaAs surface,[41–43] and the fact that only one chemical state of sulfur is observed (S 2s core-level spectrum can be curve-fitted with only one peak component at a BE of about 225.5 eV, which is associated with the sulfide species[40]), suggest that the GaAs-R^{1}OH surface consists of 6-sulfanyl-1-hexanol coupled covalently by As−S and Ga−S bonds. The thickness of the hydroxythiol layer could not be determined with sufficient accuracy by ellipsometry.

Figure 1 c shows the wide scan and Br 3d core-level spectra of the GaAs-R^{2}Br surface. The successful immobilization of the bromoester initiators on the GaAs surface is verified by the appearance of a Br 3d spin-orbit-split doublet with BEs of about 70 eV ($3d_{5/2}$) and 71 eV ($3d_{3/2}$).[40] (The BE assignments for the various elemental species and chemical states are provided in the Supporting Information.) The resulting GaAs-R^{2}Br substrate has a uniform film thickness of about 0.7 nm, as measured by ellipsometry at five different locations on the surface of a 3-cm^2 GaAs substrate. The surface roughness (R_a) of the GaAs-R^{2}Br substrate, as determined from the atomic force microscopy (AFM) image, remains practically unchanged from that of the starting GaAs surface (Table 1). The density of the coupling agent/initiator species was estimated from the linear contribution of ethyl 2-bromo-2-methylpropionate (1.33 g mL^{-1}) and 1-butanethiol (0.84 g mL^{-1}).[44] Thus, from the density (~1.1 g mL^{-1}) and the molecular weight (282 g mol^{-1}) of the coupling agent/initiator species, the surface-graft density was estimated to be about 1.6 units nm^{-2}, which is similar to that of SAMs of alkane thiols on GaAs surfaces reported previously.[37]

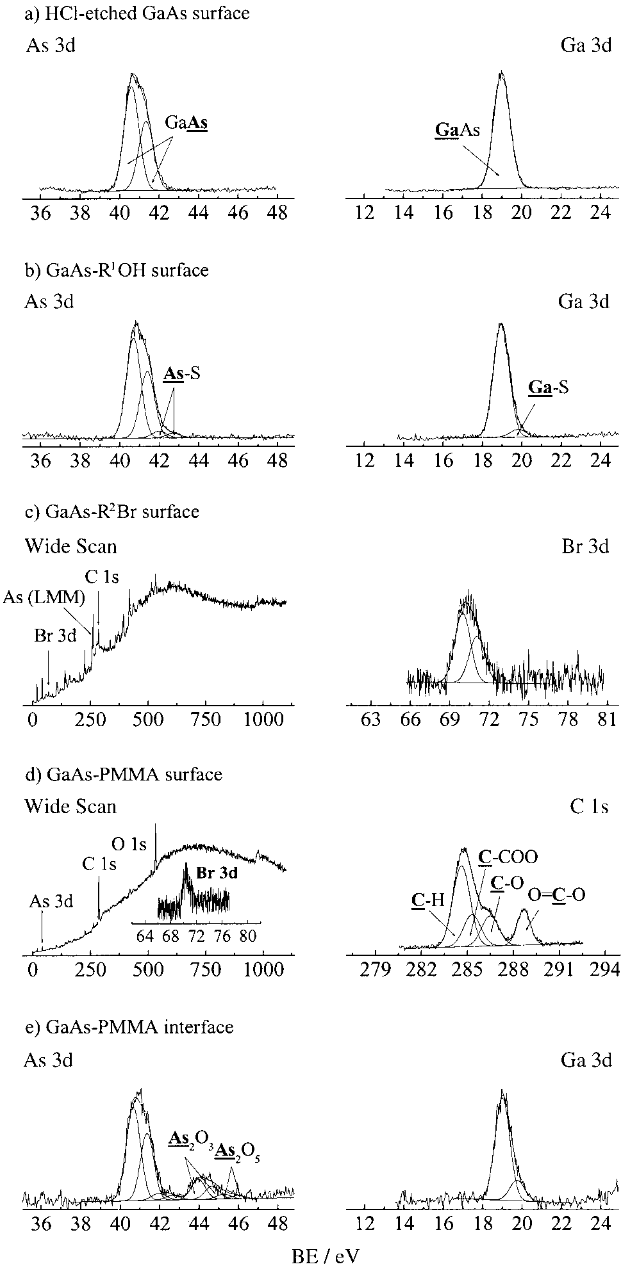

Figure 1. XPS core-level and wide-scan spectra of a) the HCl-etched GaAs surface, b) the GaAs-R^{1}OH surface, c) the GaAs-R^{2}Br surface, d) the GaAs-PMMA hybrid (sample PMMA1, Table 1) surface, and e) the GaAs-PMMA hybrid interface (sample PMMA1, Table 1).

After the surface-initiated ATRP of MMA on the GaAs-R^{2}Br surface for 21 h at room temperature, the GaAs substrate with surface-grafted MMA polymer (PMMA)—the GaAs-PMMA hybrid—was washed/extracted continuously for 8 h with a large volume of THF, which is a good solvent for PMMA, to remove the physically adsorbed PMMA and reactant residues. The resulting GaAs-PMMA hybrid, with a PMMA film thickness of about 29 nm, as measured by ellipsometry, has a water contact angle of about 69° (GaAs-PMMA4, Table 1). This contact angle is similar to

Table 1: Thickness and surface roughness of the PMMA films grafted on the GaAs (100) substrates.[a]

Sample	t [h][b]	Thickness [nm][c]	DP[d]	R_a [nm][e]
HCl-etched GaAs	–	–	–	0.56
GaAs-R^2Br	–	0.7	–	0.52
GaAs-PMMA1	4	9	120	0.43
GaAs-PMMA2	8	20	270	0.58
GaAs-PMMA3	12	24	320	0.53
GaAs-PMMA4	21	29	390	0.63

[a] Reaction conditions for fabricating GaAs-PMMA hybrids: [MMA]:[CuBr]:[$CuBr_2$]:[Me_6tren] = 500:1:0.1:1.1 at room temperature under argon. [b] Reaction time. [c] The film thickness was measured by ellipsometry. [d] The average degree of polymerization (DP) was estimated based on a surface initiator density of about 1.6 units nm^{-2}, a PMMA density of 1.1 g cm^{-3}, an MMA molecular weight of 100 g mol^{-1}, and the corresponding PMMA film thickness. [e] R_a is the arithmetic mean of surface roughness calculated from the roughness profile of the AFM image.

that of the PMMA homopolymer (about 71°).[45] As shown in Table 1, the thickness of the grafted PMMA film in the resulting GaAs-PMMA hybrids increases with an increase in polymerization time, which suggests that the growth of the PMMA chains occurs by a controlled process. This proposal was further supported by an approximately linear increase in the average degree of polymerization (DP) of PMMA homopolymer with MMA monomer conversion (see Supporting Information) for concurrent polymerizations with the free initiator (ethyl 2-bromo-2-methylpropionate) in solution. Since the average cross-sectional area of the PMMA chain prepared by surface-initiated ATRP is 1.8–2.0 nm^2[35,36] and the surface initiator density is about 1.6 units nm^{-2}, the surface initiator efficiency of the present system is estimated to be about 30%. Together with a PMMA thickness of 29 nm (sample GaAs-PMMA4, Table 1), a PMMA density of 1.1 g cm^{-3},[36] and an MMA molecular weight of 100 g mol^{-1}, the average DP of the PMMA graft chain was estimated to be about 390. This value is also similar to those obtained from homopolymerizations in solution (see Supporting Information).

XPS was again used to characterize the PMMA polymer brushes grafted onto the GaAs surface. Figure 1 d shows the high-resolution C1s core-level spectrum of the GaAs-PMMA1 sample surface (Table 1). The C1s core-level line shape is dominated by that of PMMA.[46] The spectrum consists of four peak-components with BEs at 284.6 eV for the aliphatic hydrocarbons (C–C and C–H species), 285.3 eV for the C–COO species, 286.4 eV for the C–O species, and 288.6 eV for the O=C–O species.[46] The [C–H/C–C]:[C–COO]:[C–O]:[O=C–O] molar ratio, as determined from the C1s spectral component area ratio, is 2.8:1.2:1.1:1. This ratio deviates somewhat from the theoretical ratio of 2:1:1:1 for PMMA, probably as a result of contributions of the underlying initiator and thiol coupling-agent to the aliphatic hydrocarbon species, as the PMMA film thickness (~9 nm) is comparable to the sampling depth of the XPS technique (see below). With an increase in PMMA film thickness, the surface composition approaches that of pure PMMA. The inset in Figure 1 d shows the Br3d core-level spectrum of the GaAs-PMMA1 sample surface (Table 1). The persistence of the Br signal is consistent with the fact that the growth of the PMMA chain from the surface is a surface-initiated polymerization process with a living characteristic.

The chemical states of the GaAs-PMMA hybrid interface with a PMMA film thickness of about 9 nm (sample GaAs-PMMA1, Table 1) were also investigated by XPS. Since the probing depth of the XPS technique for hydrocarbon polymers is 10 nm,[47] the As3d and Ga3d signals of the hybrid should originate mainly from the uppermost surface of the GaAs substrate after the grafting of about 9 nm of PMMA. Only a trace amount of As oxide and no Ga oxide species were observed in the XPS spectra of the GaAs-PMMA interface (Figure 1 e), which suggests that the surface-initiated ATRP has a minimal effect on the chemical states of the GaAs surface and that the surface-coupled 6-sulfanyl-1-hexanol also serves as a passivation layer for the GaAs surface.

The surface morphology of the GaAs-PMMA hybrid and the HCl-etched GaAs was studied by AFM. Figure 2 a,b show the respective AFM images of the HCl-etched GaAs and the GaAs-PMMA hybrid surfaces (sample GaAs-PMMA4, Table 1). The surface roughness (R_a ~ 0.63 nm) of the GaAs-PMMA hybrid is similar to that of the original HCl-etched GaAs surface (R_a ~ 0.56 nm). The nanoscopic uniformity of the GaAs-PMMA hybrid surface can be attributed to the well-defined PMMA brushes prepared by the surface-initiated ATRP.

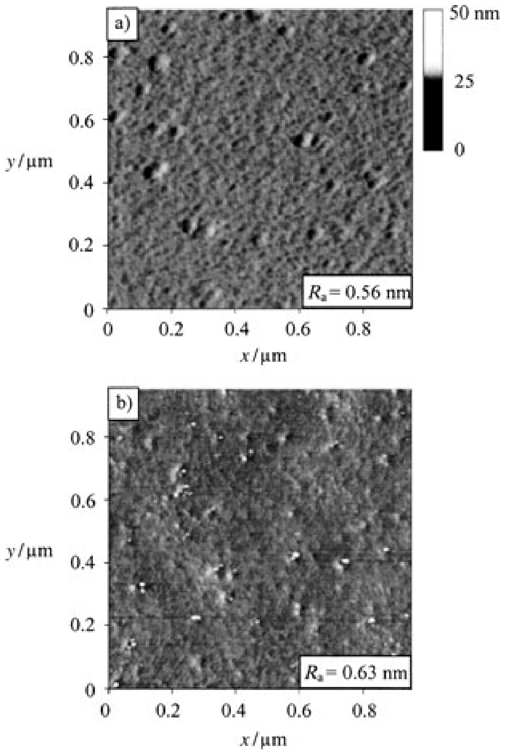

Figure 2. AFM images of a) the HCl-etched GaAs surface and b) the GaAs-PMMA hybrid surface (sample GaAs-PMMA4, Table 1).

The process of surface-initiated ATRP of MMA on the GaAs-R^2Br surface was further verified by two parallel experiments. These experiments involved 1) immersion of the GaAs-R^1OH substrate in a continuously stirred MMA monomer solution containing CuBr (14.3 mg, 0.1 mmol), $CuBr_2$ (2.2 mg, 0.01 mmol), and Me_6tren (26 µL, 0.11 mmol), and 2) immersion of the GaAs-R^2Br substrate in a continuously stirred MMA monomer solution without CuBr, $CuBr_2$, and Me_6tren, for 12 h at room temperature. No change in the thickness of the organic layer was detected by ellipsometry for samples from both experiments, which is consistent with the fact that surface-initiated ATRP of MMA occurs only in the presence of both the surface initiator and the Cu catalyst.

In summary, surface-initiated ATRP on a functionalized GaAs single-crystal surface has allowed the successful preparation of GaAs-PMMA hybrids at room temperature. The surface states of the GaAs substrate are not significantly affected by the ATRP process. The sulfanylhexanol coupling-agent acts as a covalently bonded ATRP initiator and it also passivates the GaAs surface by the formation of covalent Ga–S and As–S bonds. Thus, the present study provides a simple approach for the preparation of GaAs–polymer hybrids with well-defined polymer brushes and preserved interfacial states.

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