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Passivation of edge states in etched InAs sidewalls

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We investigate different methods of passivating sidewalls of wet etched InAs heterostructures in order to suppress inherent edge conduction that is presumed to occur due to band bending at the surface, leading to charge carrier accumulation. Passivation techniques including sulfur, positively charged compensation dopants, and plasma enhanced chemical vapor deposition of SiN_x do not show an improvement. Surprisingly, atomic layer deposition of Al_2O_3 leads to an increase in the edge resistivity of more than an order of magnitude. While the mechanism behind this change is not fully understood, possible reasons are suggested. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4986614]

In contrast to the most commonly used materials in semiconductor physics, GaAs and Si, which feature a Fermi level pinned at the mid-gap in the case of GaAs or a well-insulating native oxide layer in the case of Si, InAs shows a peculiar specialty. At the surface, its conduction band (CB) bends downward and its Fermi level is pinned above the CB minimum, which leads to an electron accumulation.[1,2] Recently, a double quantum well (QW) structure containing InAs and GaSb has been suggested as a quantum spin Hall insulator (QSHI)[3] and edge transport in etched Hall bars has been verified.[4–6] However, edge transport of a similar magnitude was also found in InAs/GaSb samples which are not in the topological phase.[7,8] The presence of this trivial edge transport and the aforementioned accumulation of charge carriers at InAs surfaces suggests that it originates from the InAs layer and is verified by observing edge transport in single InAs QWs.[9] This unwanted edge conduction can not only obscure data in the intricate InAs/GaSb material system but is also detrimental to realizing quantum devices in InAs heterostructures, as mesa edges and structures defined by etching introduce a parallel conducting channel and InAs nanowires, where surface accumulation is believed to drastically lower the mobility at low temperatures.[10,11] In recent work, these problems could be controlled for field effect transistors (FETs), displaying promising room temperature operation of devices in industry dimensions.[12–14]

In this paper, we investigate InAs Hall bars which display edge conduction after the bulk is pinched off by top-gating and apply different passivation techniques during fabrication with the goal of alleviating this edge conduction. Our heterostructure is grown by molecular beam epitaxy (MBE) on a GaAs substrate and consists of 200 nm GaAs, followed by 6 nm AlAs, a 32 nm AlSb layer, a 1100 nm $Al_xGa_{1-x}Sb$ layer ($x = 65\%$), a 500 nm GaSb layer, a 50 nm superlattice of 10 iterations of 2.5 nm AlSb and 2.5 nm GaSb layers, and then the 15 nm InAs QW sandwiched by two 50 nm AlSb barriers and a 3 nm GaSb capping layer to prevent the oxidation of the barrier. Ohmic contacts (Ge/Au/Ni/Au) have been evaporated, and $4 \times 8\,\mu m$ Hall bars were defined using standard wet etch recipes.[15,16] Following the etching process and resist removal in acetone and isopropanol, different passivation techniques have been applied, which consisted either of a chemical dip and dielectric deposition or the direct deposition of a dielectric. This separates the structure from the subsequently evaporated Ti/Au top gate. As InAs/GaSb heterostructures have widespread use in infrared detection where surface accumulation can lead to unwanted signals, different passivation techniques have been explored for optoelectronic devices.[17] A range of these are applied to transport measurements in the following. The most widespread technique is sulfur passivation using either ammonium sulfide,[18] thioacetamide (TAM),[19] or 1-octadecanethiol (ODT).[20,21] The general idea behind this method is the creation of covalent bonds to a layer of sulfur adatoms, reducing the density of surface states. For the ammonium sulfide passivation, samples are dipped in a 20 % $(NH_4)_2S$ solution at room temperature for up to 15 min. As can be seen in Fig. 1(f), this chemical is too aggressive and etches parts of the heterostructure, presumably the AlSb barriers. This leads to visible "lifting off" of parts of

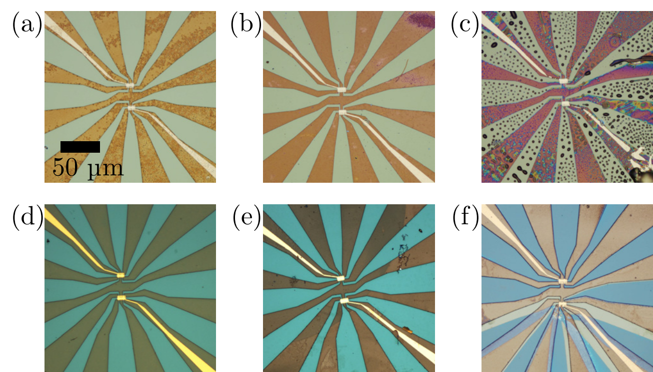

FIG. 1. Optical microscopy images of a selection of samples, displaying visual changes of different passivation techniques employed: (a) no treatment after etching, deposition of 150 nm SiN_x by PECVD; (b) immersion in $Mg(BH_4)_2$, subsequent SiN_x deposition; (c) treatment with PCBM, subsequent SiN_x deposition; (d) no treatment after etching, deposition of 40 nm Al_2O_3 by ALD; (e) immersion in TAM followed by Al_2O_3 deposition; and (f) immersion in ammonium sulfide followed by Al_2O_3 deposition. The scale bar applies to all images (a)–(f).

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the mesa structure and results in nonfunctional devices whose transport behavior does not depend on gate voltages and magnetic fields in a way characteristic for two-dimensional electron gases. Reducing the dip time and diluting the solution further (up to 1 : 4) in H_2O did not resolve this problem, which renders ammonium sulfide unsuitable for our purpose. A second, more gentle form of sulfur passivation is investigated by using TAM in H_2O at a concentration of 0.2 mol/l, at a temperature of 60 °C and at a pH of 2 which was adjusted by adding acetic acid, following Petrovykh *et al.*[19] The time of the dip was again varied up to 15 min and did influence neither the resulting data nor the visual appearance of the sample [compare Fig. 1(e)]. Additionally, we explore two other methods of passivation in magnesium borohydride ($Mg(BH_4)_2$) and phenyl-C61-butyric acid methyl ester (PCBM). $Mg(BH_4)_2$ is intended to reduce native and other oxides after wet etching and then to terminate the surface with Mg^{2+}, thereby acting as a "compensation doping" for the surplus of negative charge carriers at the surface. PCBM, which is a known electron acceptor in organic photovoltaics, could also act as an acceptor for these charges. $Mg(BH_4)_2$ was dissolved in tetrahydrofuran (THF) in a glovebox at an argon atmosphere, into which the samples had been introduced before. The samples were then dipped into the solution for 2 min at room temperature and at 60 °C. No influence of the temperature could be determined. This treatment also preserved the sample quality, as can be seen in Fig. 1(b). Performing a dip was not possible for PCBM. Therefore, using a pipette, a toluene solution of PCBM was dropped onto the sample lying on a hotplate in the glovebox. This technique unfortunately resulted in very uneven spatial distribution and the formation of small droplets, which can be seen in Fig. 1(c). They made subsequent cleanroom fabrication unfeasible. The sample shown featured the smallest amount dropped (5 μl) and was the only one where a working gate could be fabricated, albeit with a very limited tuning range, as will be discussed later. Two other kinds of samples have not been chemically passivated but were solely overgrown with 150 nm SiN_x by plasma enhanced chemical vapor deposition (PECVD) at a temperature of 300 °C or 40 nm Al_2O_3 by atomic layer deposition (ALD) at a temperature of 150 °C. Another sample was etched and then left at a cleanroom air atmosphere for two weeks before continuing fabrication (with an ALD Al_2O_3 gate dielectric) in order to investigate oxidized edges. They are believed to be conducting, although experimental data on their transport behavior have not been reported in the literature so far.

In Fig. 2, we show transport data comparing the previously described methods of passivation. The longitudinal resistance R_{xx} of Hall bars, measured by low frequency AC lock-in techniques at $T = 1.3$ K, is plotted as a function of effective density n_{eff}. This quantity has been calculated by determining the relationship between electron density n in the QW and the top gate voltage, V_{tg}, from Hall effect measurements and extending the scale linearly to negative gate voltages. We want to emphasize that only $n_{\mathrm{eff}} \geq 0$ has a physical meaning corresponding to the density in the QW, and negative values merely provide a renormalized gate voltage axis which is independent of different capacitances and charge redistributions. From Corbino disk measurements in InAs, it is known that the QW can be completely depleted by a top gate, driving the resistance in the bulk of the device to arbitrarily high values, whereas for Hall bars with etched edges, it saturates in the kΩ range.[9] A successful passivation is therefore expected to either completely suppress the edge conduction, facilitating insulating behavior after QW pinch-off, or at least increase their resistance to a value high enough to unambiguously observe ballistic transport phenomena in InAs-based material systems, i.e., $R_{\mathrm{edge}} \gg \frac{h}{e^2}$ for typical edge lengths. Turning to Fig. 2, we can immediately distinguish two different families of curves. For samples, passivated with TAM, $Mg(BH_4)_2$, SiN_x, and the oxidized sample, R_{xx} saturates between 3–14 kΩ. This allows us to draw the following conclusions: first, our measurements are consistent with the results of Ref. 9, where the edge conductance of the same order of magnitude was measured in PECVD SiN_x overgrown Hall bars. Second, the presumption that oxidized samples display edge conduction is correct, and its magnitude is similar to samples which have been overgrown by PECVD directly after etching and therefore have not been purposely oxidized. Here, it is important to mention that the exact dynamics of the oxidation process are not well understood, which means that edges could already start to oxidize during resist removal necessary after wet etching and the transfer time to the vacuum chamber for dielectric deposition. Third, neither the sulfur passivation with TAM nor the $Mg(BH_4)_2$ dip led to a significant change in transport behavior after pinch-off.

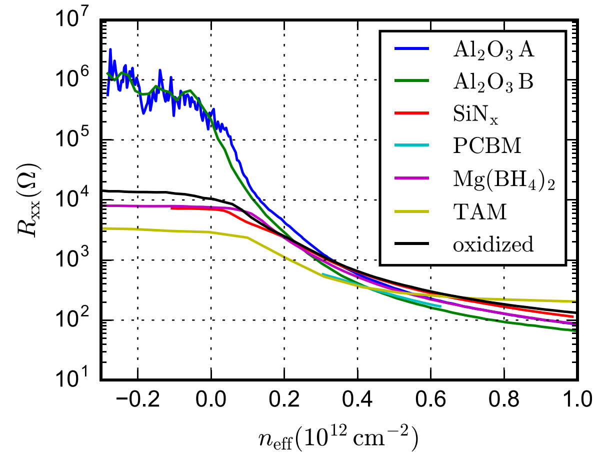

FIG. 2. Longitudinal resistances R_{xx} of Hall bars passivated by different techniques as a function of effective density n_{eff}, obtained by extending a linear fit of the gate voltage to density characteristic to negative voltages. The positive values of this quantity correspond to the density in the quantum well, while negative values provide a renormalized gate voltage axis, allowing comparison of devices with different gate dielectrics and thicknesses. ALD Al_2O_3 samples shown are passivated directly after wet etching (A) and with 1 h of waiting time (B).

The two types of samples fabricated without chemical passivation and ALD Al_2O_3 display a resistance increasing to MΩ after depletion of the QW, which is surprising as one would naively expect the water precursor of the ALD process to further edge oxidation. After pinch-off, the resistance slightly increases with decreasing gate voltage and develops more noise. These fluctuations do not reproduce exactly in subsequent measurements. They lead us to believe that the carrier accumulation at the edge is sufficiently reduced such that transport is close to breaking down. Sample B, which

was left in air for approximately 1 h during chemical passivation of other samples and was intended as a reference sample, surprisingly first showed the enhanced resistance. After this observation, the process was repeated without waiting time (sample A), displaying a further increase in the resistance. Therefore, we recognize that the oxidation process is happening on timescales slower than 1 h but faster than two weeks (c.f. oxidized sample, black curve in Fig. 2). Finally, the data of the PCBM passivated sample (cyan curve in Fig. 2) show a tuning range limited by gate leakage which occurred due to the severe fabrication difficulties described previously. Of four devices, only one functioned, rendering PCBM unsuitable as a method of passivation. While the data in Fig. 2 show the resistance across the whole device, it has been verified by nonlocal transport measurements that the current flows along the edge for gate voltages below pinch-off and that there are no other bulk leakage paths that the current can take after the QW is pinched off.

Using a resistor network model shown in the inset of Fig. 3, it is possible to calculate a specific edge resistivity λ_{edge}. The assumptions in this model are a complete QW pinch-off, current flowing entirely along the edges, and an edge resistance that scales linearly with the edge length. As previously mentioned, the first two assumptions are justified by Corbino disk and nonlocal measurements, whereas the last one is expected for a diffusive conduction path along the edge and is confirmed in our measurements. The specific value of λ_{edge} depends on the point chosen for analysis in the region where the QW is pinched off. This is because the edges can be gated weakly, resulting in a finite slope after the depletion of the QW, which can be seen in Fig. 2. For consistency, we have evaluated the edge resistivity at the point $n_{eff} = 0$ for all samples. The comparison of λ_{edge} for all feasible passivation techniques used is displayed in Fig. 3, where λ_{edge} of the ALD Al_2O_3 passivation exceeds all other passivation techniques by more than an order of magnitude.

The role of the ALD Al_2O_3 process in controlling the surface states of etched InAs heterostructures can be rationalized as follows: The trimethylaluminum, $Al(CH_3)_3$, precursor used in the ALD process can act as a powerful reducing agent, which is known as self-cleaning.[22] As an example, $Al(CH_3)_3$ has been shown to remove native oxides from the surface of GaAs.[23–25] There are also reports on surface reduction of InAs and InAs/GaSb heterostructures with $Al(CH_3)_3$.[26–29] The reduction of native oxides is essentially already complete after the first $Al(CH_3)_3$ pulse in the ALD process.[30] After the native oxides are reduced, only Al_2O_3 forms as it has a much lower Gibbs free energy of formation ($-377.9\,\text{kcal/mol}$)[31] as compared to all other possible oxides on the surface of InAs (the Gibbs free energies of In_2O_3, As_2O_3, and As_2O_5 are $-198.6\,\text{kcal/mol}$, $-137.7\,\text{kcal/mol}$, and $-187.0\,\text{kcal/mol}$).[27] This strong chemical reducing capability of $Al(CH_3)_3$ under ALD-conditions has been reported also for other systems.[32,33]

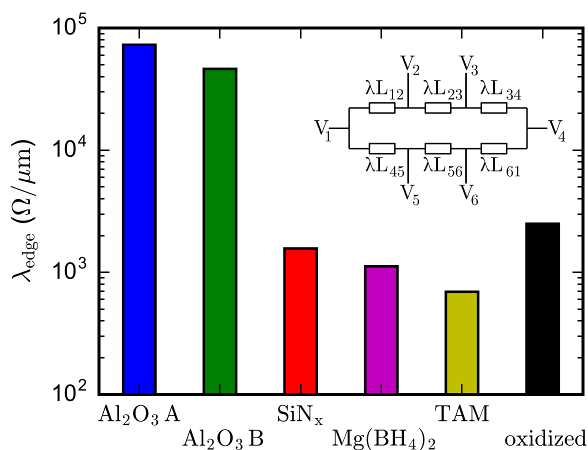

FIG. 3. Bar chart comparing specific edge resistivities λ_{edge} of different passivation techniques. All methods investigated in this paper display $\lambda_{edge} < 2.5\,\text{k}\Omega$, with the exception of ALD Al_2O_3, where λ_{edge} reaches $72.8\,\text{k}\Omega$. Inset: the resistor network model used to calculate the specific edge resistivity.

A possible reason for the ineffectiveness of sulfur passivation could be the fact that, as a group VI element, it provides an additional electron and can act as a donor, which in a different context has been reported to increase band bending at the surface.[34,35] This is also true for the related group VI element selenium.[36] For transport applications, this effect seems to outweigh the advantages of terminating etched surfaces reported in optoelectronics.[17] This motivated the use of $Mg(BH_4)_2$ and PCBM to counter-dope at the surface, which, disregarding fabrication difficulties for PCBM, was not effective. Possible reasons could be too low or too high concentrations or the usage of an unsuitable chemical, which cannot be narrowed down at this point.

In conclusion, different methods to passivate edge states in transport through etched InAs QW structures have been investigated of which ALD Al_2O_3 has been determined as the most effective technique, with a specific edge resistivity of up to $\lambda_{edge} = 72.8\,\text{k}\Omega/\mu\text{m}$. While edge conductance could not be removed completely, we hope that our findings are sufficient to stimulate research and applications in InAs and InAs-based materials and contribute to discussions on edge states in these systems. As an outlook for further efforts in passivation, finding a suitable chemical is still an open question. Another feasible option could be the passivation by MBE overgrowth with related materials of larger band gap, such as a quaternary alloy.[37]

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