Epitaxial liftoff of ZnSe-based heterostructures using a II-VI release layer

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Epitaxial liftoff is a post-growth process by which the active part of a semiconductor heterostructure, the epitaxial layer, is removed from its original substrate and deposited onto a new substrate. This is a well established technique in GaAs-based heterostructures where epitaxial liftoff can be achieved by exploiting the contrast in the etch rates of GaAs and AlAs in hydrofluoric acid. We report here successful epitaxial liftoff of a ZnSe-based heterostructure. We find that a metastable layer of MgS acts as a perfect release layer based on the huge contrast in the etch rates of ZnSe and MgS in hydrochloric acid. Epitaxial liftoff of millimeter-sized ZnSe samples takes a fraction of the time required for GaAs liftoff. Photoluminescence experiments confirm that the liftoff layer has the same optical characteristics as the original wafer material. © *2005 American Institute of Physics.*
[DOI: 10.1063/1.1844595]

The development of heterostructures has revolutionized both the physics and the technology of semiconductors. Inherent to the technique is the growth of high quality semiconductor layers on a single crystal substrate. The substrate must be of high crystal quality with a lattice constant similar to that of the epitaxial layer itself. In some cases, these conditions impose unwelcome restrictions on the range of heterostructures that can be produced. Also, for some technologies, for instance solar cells, a single crystal substrate is simply too expensive. Epitaxial liftoff is a technique which can add flexibility to the fabrication of semiconductor devices.[1] It allows the epitaxial layer to be removed from its substrate in a post-growth processing step so that the epitaxial layer can be deposited onto a new substrate with different functionality. The liftoff step also allows the original substrate to be reused.

Up until now, epitaxial liftoff has been achieved using the remarkable contrast in the etch rates of GaAs and $Al_xGa_{1-x}As$ in HF.[2,3] For $x \geq 0.5$, the Al-containing alloy etches many orders of magnitude faster than GaAs. Epitaxial liftoff of a GaAs-based heterostructure can therefore be achieved by growing a thin sacrificial layer of AlAs between the substrate and the active layer. A sacrificial layer of thickness between 3 and 40 nm is effective.[4] After growth a wafer piece is submerged in HF, the HF etching through the AlAs layer but having a negligible effect on GaAs, InGaAs, and low Al-content AlGaAs alloys. In addition to the etch selectivity, a crucial idea is to stress the epitaxial layer so that as the etching proceeds, the epitaxial layer curls up slightly.[3] This is important as otherwise the etching would proceed too slowly and eventually stop altogether. The stress can be applied by several methods, the simplest of which is to anneal a layer of wax.[2,3] This idea has been used to lift crack-free layers as thin as 20 nm from the original substrate.[5] This technology has been exploited in a number of semiconductor devices. A laser diode,[6,7] a solar cell,[8] rib waveguides,[9] and a photodetector[10] have all been transferred onto a foreign substrate. Attempts have been made to speed up the process, and to make it compatible with industrial scale semiconductor processing in order that epitaxial liftoff also becomes a commercially viable technology.[1,4]

Despite recent progress, epitaxial liftoff remains a possibility only for GaAs-based heterostructures. While InP-based and ZnSe-based layers have been lifted from their original substrates,[4,11] in both cases the technology depends on an AlAs release layer. In the case of II-VI materials, this is inconvenient as it not only increases the thickness of the epitaxial layer which can be lifted off but it also requires both III-V and II-VI molecular beam epitaxy. The absence of a viable technique for carrying out II-VI epitaxial liftoff is a serious limitation in at least two areas. First, while Bragg stacks can be grown in a GaAs-based heterostructure by exploiting the difference in refractive index between the lattice-matched pair, GaAs and AlAs, there is no lattice-matched pair of II-VI materials with sufficiently different refractive indices. Epitaxial liftoff would provide a natural way in which thin high quality ZnSe layers could be transferred onto a conventional dielectric Bragg mirror. This is important for polariton parametric amplification,[12,13] a very attractive concept for ZnSe quantum wells where excitons can be stable up to high temperatures.[14] Second, magnetic atoms can be incorporated into II-VI compounds without introducing any doping and this is driving the interest in II-VI materials for spintronics applications.[15] Epitaxial liftoff could offer valuable advantages in combining this property with ferromagnetic layers.[16]

We present a method of performing epitaxial liftoff of ZnSe-based heterostructures. We have discovered that a thin layer of MgS in a ZnSe-based heterostructure acts in an analogous way to AlAs in a GaAs-based heterostructure. Bulk MgS exists in the rock-salt crystal structure but we are able to grow layers up to 134 nm thick in the zinc-blende structure on a GaAs substrate.[17] Up to this thickness, the layer quality is very high as can be judged from the excellent optical properties of ZnSe/MgS quantum wells.[14] At larger thicknesses, the MgS layer reverts back to the rock-salt structure and further zinc-blende growth is clearly of low quality. We exploit here the pronounced difference in chemical properties between MgS and ZnSe to perform epitaxial liftoff. Remarkably, we find that the etch rate of a MgS layer is $\sim 10^8$ times larger than the etch rate of a ZnSe layer.

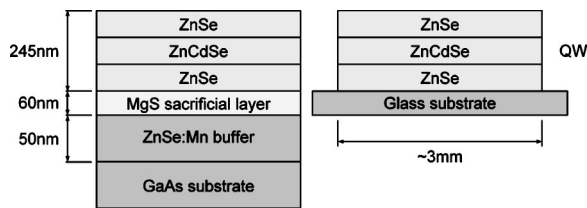[a]Electronic mail: a.curran@hw.ac.uk

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FIG. 1. Left-hand side: heterostructure for the II-VI epitaxial liftoff experiment. The sacrificial layer is the MgS layer, on top of which is a ZnCdSe/ZnSe quantum well. Right-hand side: schematic of the lifted quantum well (QW) bonded, via the van der Waals force, to its new substrate, in the present case a polished glass substrate.

The heterostructure for these experiments was grown by MBE on a GaAs n^+-substrate. We deposit first a 50 nm ZnSe buffer followed by the 60 nm MgS sacrificial layer.[17] The buffer was alloyed with a small concentration of Mn impurity atoms as we use the deep level emission from excitons bound to Mn impurities as a marker in the photoluminescence experiments. A ZnCdSe/ZnSe quantum well is grown on top of the MgS, with barrier thicknesses 120 nm, quantum well thickness 5 nm and Cd concentration of $\sim 10\%$. The overall strain in the heterostructure is kept sufficiently low in order to prevent strain relaxation through dislocation formation. We note that the zinc-blende MgS layer is helpful in reducing the overall strain, as its lattice constant, 0.5622 nm,[17] is smaller than that of GaAs, 0.5653 nm,[18] whereas the ZnSe lattice constant, 0.5668 nm,[18] is larger. The in-plane lattice constant of the entire heterostructure is determined by the GaAs substrate. The MgS layer can therefore provide some strain compensation for the subsequent growth of ZnSe. A detailed layer structure of the heterostructure is shown in Fig. 1.

In order to perform the epitaxial liftoff, we cleaved samples $\sim 3 \times 3$ mm^2 in size from the wafer material, taking considerable care to get perfect cleaves. The surface was then coated with Apiezon wax at room temperature and annealed at 80 °C, the technique developed for GaAs-based liftoff.[3] However, instead of HF, we use HCl with a concentration of 30% for the etch. MgS reacts with HCl to form MgCl$_2$ and H$_2$S, both of which are water soluble up to high concentrations. Conversely, the other layers in the heterostructure, ZnSe and ZnCdSe, are etched at a much slower rate by HCl. The wax-coated samples were placed face up in the HCl at room temperature. Typically the epitaxial layer released from the substrate within about 30 min. As is the case in GaAs-based liftoff, the wax-coated epitaxial layer floated to the surface, leaving the GaAs substrate behind.

We estimate that the etch rate of the MgS release layer is about 3 mm/h. This is considerably larger than the etch rate of AlAs release layers in GaAs-based liftoff. Using the wax technique, the AlAs release layer etch rate is ~ 0.3 mm/h,[3] and has been increased to 1 mm/h by increasing the temperature.[19] It has been argued that the limiting step in AlAs etching is the solubility of H$_2$ gas which is one of the reaction products.[3] The etching cannot be accelerated without H$_2$ gas coming out of solution, which leads to the formation of bubbles and cracks in the epitaxial layer. In our case, the etching rate is considerably faster and this is in all probability related to the high solubility of the reaction products.

The epitaxial lift off technique relies on a large contrast in the etch rates of the sacrificial and active layers. We have measured the etch rate of ZnSe in the HCl etchant used for the liftoff by exposing part of the surface of a ZnSe epitaxial layer to the acid, protecting the other part of the surface with photoresist. After removing the photoresist, we measured the etched depth with an atomic force micrograph. Even after several days in the etchant, the ZnSe etch depth was only a few nm. By comparing the etch rate of the MgS sacrificial layers in the liftoff process with this measurement, we can conclude that the contrast in etch rates between MgS and ZnSe in HCl is $\sim 10^8$.

After etching through the sacrificial MgS layer, the epitaxial layer was transferred onto a glass substrate by applying a small force and it was found that the epitaxial layers are strongly bonded to the glass substrate. No adhesive was used. The bonding between epitaxial layer and substrate is most likely through the van der Waals interaction.[5] The surface of the glass substrates are optically flat (surface roughness less than a quarter wavelength at 633 nm). After overnight drying, the wax was removed by dissolving it away in warm trichloroethylene. This left a 245 nm thick ZnSe epitaxial layer on the glass substrate. The epitaxial layers were crack-free over square millimeter areas. The liftoff layers are not completely perfect but the defects are mostly related to the presence of small dust particles on the substrate surface and so the quality could be much improved by working in a cleaner environment (our liftoff experiments were conducted in a laboratory with an unfiltered air supply).

In order to probe the quality of the liftoff layers, we performed photoluminescence spectroscopy on both the original wafer material and on an epitaxial layer on a glass substrate. Photoluminescence was excited by a GaN laser diode emitting at 400 nm. A few hundred μW of power was focussed to a spot size of ~ 10 μm with a $\times 5$ microscope objective. The same objective collected the photoluminescence which was focused into a grating spectrometer with a multichannel liquid-nitrogen-cooled charge-coupled-device camera as a detector. Results taken at room temperature are presented in Fig. 2. The wafer material exhibits three photoluminescence features. The strongest peak at 2.54 eV (487 nm) arises from emission between the lowest electron state and lowest hole state in the quantum well. The spectrally sharp emission at 2.69 eV (460 nm) is identified to be emission from the bulk ZnSe layer. The broad emission at low energy (high wavelength) arises from Mn-related emission. Figure 2 also shows photoluminescence collected from the epitaxial layer on a glass substrate. The excitation power and the optical alignment remained the same for the two samples in order to facilitate a comparison. Figure 2 shows that the luminescence efficiency of the quantum well is not changed within the measurement uncertainty of about 10% by the liftoff procedure. This is a very positive result. Furthermore, the photoluminescence curves peak at energies (wavelengths) which differ by at most 6 meV (1 nm). This shows that the strain in the quantum well is largely unchanged on lifting off the epitaxial layer. The broad emission around 2.3 eV (540 nm) is considerably weaker in the liftoff layer photoluminescence than in the wafer material photoluminescence. This is exactly as expected as the buffer layer is no longer present in the epitaxial liftoff layer.

In conclusion, we present the successful epitaxial liftoff of a II-VI epitaxial layer using a II-VI release layer, a metastable MgS layer. The liftoff depends on a huge difference between the etch rates of MgS and ZnSe in HCl. We have demonstrated that liftoff proceeds more rapidly with a MgS
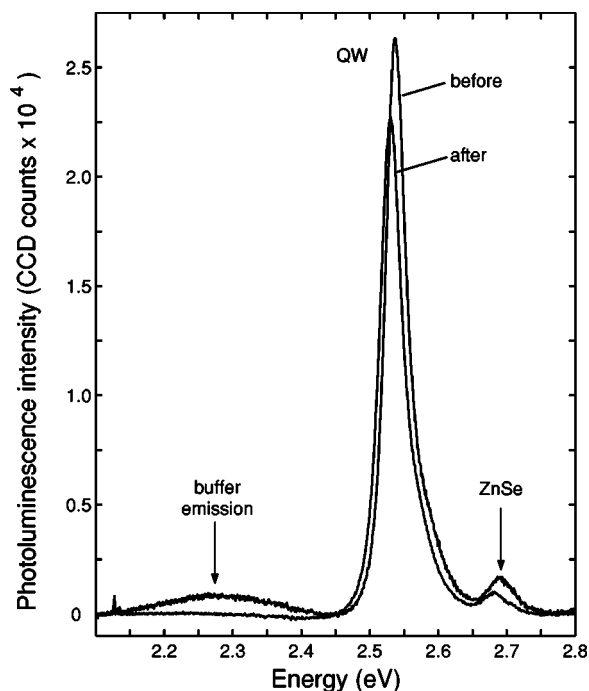
FIG. 2. Photoluminescence at room temperature from the ZnCdSe/ZnSe quantum well both before and after the liftoff process. The excitation was provided by a GaN laser diode emitting at 400 nm.

release layer than with the conventional AlAs release layer in the III-V system. This result is potentially very important as it allows the attractive properties of II-VI quantum wells, strong excitonic emission in the visible with enhanced spin effects through the incorporation of magnetic impurities, to be combined with a functionalized substrate.

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