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Extreme selectivity in the lift-off of epitaxial GaAs films

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We have discovered conditions for the selective lift-off of large area epitaxial $Al_x Ga_{1-x}As$ films from the substrate wafers on which they were grown. A 500-Å-thick AlAs release layer is selectivity etched away, leaving behind a high-quality epilayer and a reusable GaAs substrate. We have measured a selectivity of $\gtrsim 10^7$ between the release layer and $Al_{0.4}Ga_{0.6}As$. This process relies upon the creation of a favorable geometry for the outdiffusion of dissolved H_2 gas from the etching zone.

In thin-film technology there has always been a trade-off between the material quality of the film and the ease of depositing that thin film. Epitaxial films represent the highest level of quality, but they must be grown on and are accompanied by cumbersome, expensive, bulk single-crystal wafer substrates. For some time[1] research has focused on the possibility of creating epitaxial quality thin films on *arbitrary* substrates while maintaining the ultimate in crystalline perfection.

The main approach has been to regard the substrate wafer as a kind of reusable epitaxial growth template which could then be physically separated from the epitaxially grown film. For example Fan[1] has promoted a process in which an epitaxial film is cleaved away from the substrate on which it is grown. In a little noticed paper[2] almost ten years ago, Konagai *et al.* showed that there was excellent selectivity in etching and undercutting the $Al_x Ga_{1-x}As$ alloys in hydrofluoric[3] acid. They called this peeled film technology and demonstrated 30-μm-thick solar cells, but they did no further work in this area. Later it was pointed out[1] that the main problem with any such etching process is the need to circulate the reactants and the reaction products in and out of the small crevice formed between the film and the substrate.

We have discovered conditions for the selective lift-off of large area epitaxial $Al_x Ga_{1-x}As$ films ($x \leqslant 0.4$) from the substrate wafers on which they were grown. A typical epitaxial layer test structure is shown in Fig. 1. The epitaxial film is simply undercut and lifted off its growth substrate. Two key elements make such a process work:

(i) To undercut a very thin film over its entire area the selectivity must be extremely high. We have measured a selectivity of $\gtrsim 10^7$ between the AlAs release layer and $Al_{0.4}Ga_{0.6}As$, with the onset of etching occurring very suddenly between 40 and 50% aluminum composition. We do not understand this remarkable selectivity, but we propose to take full advantage of it.

(ii) The critical reaction product in semiconductor etching is dissolved hydrogen gas. The geometry of Fig. 1 is actually impractical. The gas is unable to diffuse out through such a narrow channel as represented by the thin release layer channel in Fig. 1. The gas comes out of solution, forming a bubble which displaces the etchant before the film has been undercut very far. As suggested by Fan,[1] this problem may have stymied Konagai *et al.*[2] In this letter we describe a film geometry which overcomes this serious difficulty.

In our work we employed contactless minority-carrier lifetime decay[4] as a diagnostic probe of the material quality and the etching characteristics. In the double heterostructure configuration shown in Fig. 1, the minority-carrier lifetime can be very long.[5] A surface layer of $Al_x Ga_{1-x}As$ as thin as 100 Å is able to confine the minority carriers within the GaAs potential well. When the upper $Al_x Ga_{1-x}As$ layer is etched away, the minority-carrier lifetime becomes very short due to surface recombination.[4] Therefore, such a layer structure permits a very sensitive measure of very tiny etch rates.

By monitoring the minority-carrier lifetime of a GaAs potential well capped by thin $Al_x Ga_{1-x}As$ layers as a function of etch time and of composition x, we could determine some of these important parametric dependences. We found that the etch rate of $Al_{0.4}Ga_{0.6}As$ in concentrated (48%) HF acid could be very slow, only ≈ 1.5 Å per hour, at room temperature[6] and even slower at 0 °C. We must assume that the etch rate of pure GaAs is yet again slower. By contrast, an increase in aluminum concentration from 40 to 50% increases the etch rate by many orders of magnitude. Based upon the speed at which the AlAs release layers are undercut, the etch rate can be as high as 1 mm per hour (roughly proportional to HF acid concentration). Such a degree of selectivity ($\gtrsim 10^7$) might be associated with percolation type behavior[7] or possibly a shift from Γ minimum to X-point minimum in the band structure. In optimizing the lift-off process we standardized the release layer composition to

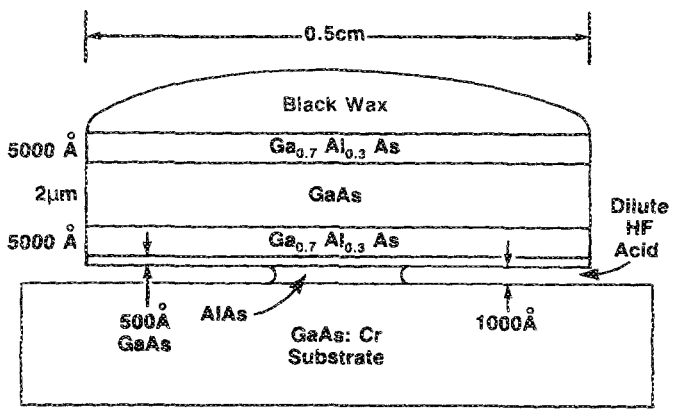

FIG. 1. Macroscopic epitaxial films can be undercut by dilute hydrofluoric acid. The AlAs release layer is shown as 1000 Å thick but has been as thin as 20 Å. In actual practice, the tension in the wax supporting layer lifts up the edges of the film as shown in Fig. 3.

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pure AlAs but $Al_{0.5}Ga_{0.5}As$ release layers were equally successful.

The films were grown on ⟨100⟩ oriented GaAs substrates by molecular beam epitaxy and organometallic chemical vapor deposition. The superb electronic quality of epitaxially grown films is unaffected by the lift-off process. This may be seen from the minority-carrier lifetime decay curves shown in Fig. 2. Minority-carrier lifetime is one of the best measures of crystalline perfection and purity. The test structure shown on Fig. 1 was monitored by the contactless lifetime probe described in Refs. 4 and 5. For comparison, the carrier density decay curve was measured before lift-off and then again after lift-off. The two decays overlay identically so there is only one curve actually shown in Fig. 2. The initial rapid decay is due to radiative electron-hole recombination, and the slow decay at lower density measures the Shockley–Read–Hall lifetime.[5]

We have lifted off crack-free GaAs films as thin as 800 Å and as large as 0.8 cm × 2.5 cm. Needless to say, such films are very fragile and must be supported at all times. The initial mechanical support during and after lift-off comes from the black wax shown in Fig. 1. This is not actually wax but is rather a proprietary mixture known as Apiezon W. We believe that the key factor in the success of our process lies in the tension induced in this waxlike material. The curing and annealing conditions adjust the tension of the wax to ensure that as the GaAs film becomes undercut it curls up slightly with a radius of curvature R as shown in Fig. 3. Therefore, the wax is under tension and the GaAs is under compression. Mechanically this is beneficial since GaAs, like most materials, is much stronger in compression than in tension. The real reason for doing this though, is the slight up-lifting of the corners of the GaAs film (shown out of proportion in Fig. 3) which permits the reaction products of etching, in particular dissolved H_2 gas, to diffuse from the etching zone without coming out of solution. Typically, after such a sample has been sitting in HF acid for 24 h the GaAs film supported by the wax simply floats off.

In our process, a solution of 25 g wax dissolved in 100 ml trichloroethylene is sprayed onto the GaAs wafer through a

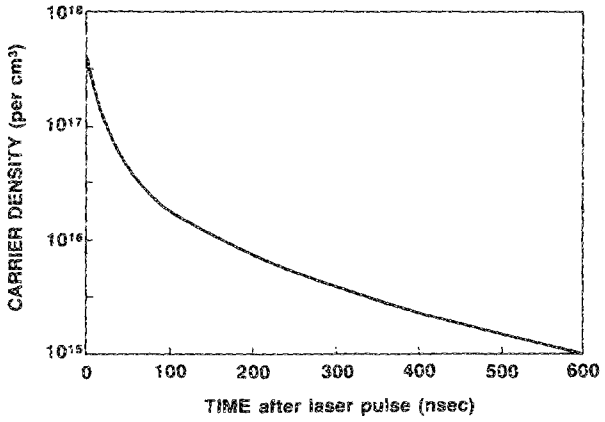

FIG. 2. Minority-carrier lifetime decay curve of the double heterostructure shown in Fig. 1, both before and after lift-off from the substrate wafer. Only one curve is shown since the two curves were indistinguishable. The initial rapid decay is due to radiative recombination while the slow decay at lower density measures the crystallographic quality in terms of Shockley–Read–Hall lifetime.

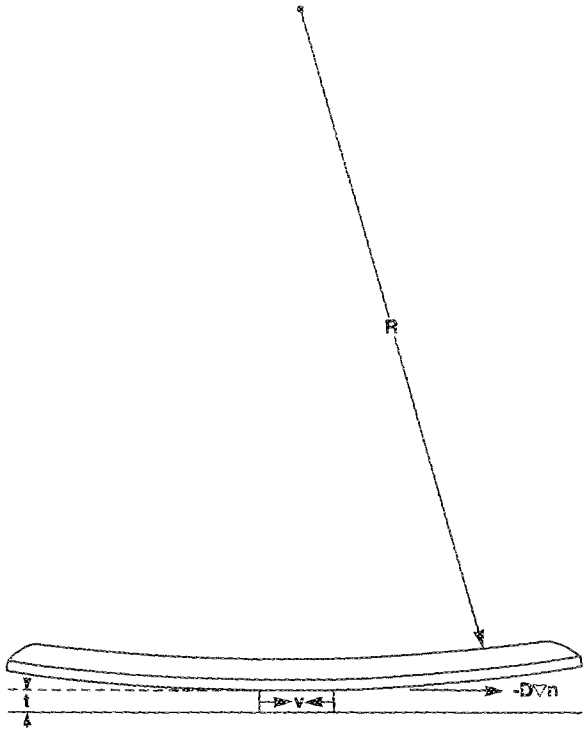

FIG. 3. Tension in the wax is controlled so as to lift up the corners of the epitaxial film during undercutting. This permits the outdiffusion from the etching zone of dissolved H_2 gas, the most critical reaction product. The relative proportions of thickness and curvature are greatly distorted in this depiction. The diffusion flux of dissolved H_2 is represented by $-D\nabla n$.

shadow mask (several times to build up the thickness). It is then air cured for 1/2 h and annealed at 100 °C for 1/2 h. This seems to produce the right amount of tension and curvature for a GaAs (or $Al_xGa_{1-x}As$) film about 1 μm thick. The epitaxial layer edges around the wax are then exposed and the sample placed in HF acid. Since H_2 gas has the lowest solubility of any of the reactants or reaction products, the ability to diffuse away the dissolved gas limits the undercutting speed and therefore the permissible HF acid concentration. If the limits are exceeded, bubbles will come out of solution at the reaction zone displacing the etchant. Whenever we exceed this threshold acid concentration, the hydrostatic pressure of the gas bubbles cracks the film in uniform rings that move in from the periphery. Therefore, we typically restrict the HF acid concentration to ~10% to limit the etching speed. The maximum permissible speed of undercutting may be calculated for the case of a plane parallel etching channel. Equating first the diffusion flux with the etching flux:

$$v t\, 3N = -Dt\frac{dn}{dz}, \tag{1}$$

where v is the etching speed, n and N are the molar concentrations of dissolved H_2 gas and AlAs, respectively, t is the thickness of the channel, D is the diffusion constant of the H_2 gas, and z is the position coordinate down the channel. It is assumed that 3 moles of H_2 gas are produced for every mole of AlAs. The thickness cancels from both sides of Eq. (1) showing that, contrary to intuition, a thick release layer does not overcome the mass transport problem since proportion-

ately more H_2 must be removed. Integrating Eq. (1) down a plane parallel channel of depth L results in a maximum undercutting speed v:

$$v = Dn/3LN, \tag{2}$$

where n is now the saturation solubility of the H_2 gas. Since[8] n/N is $\sim 2\times 10^{-5}$ and D in aqueous[9] media $\sim 5\times 10^{-5}$ cm^2/s, the speed is severely limited in channels of any significant depth. If the channel opens up as shown in Fig. 3, then the outdiffusion becomes much easier. Equating again, the etching flux with the diffusion flux becomes

$$vt\,3N = -D\left(t + \frac{z^2}{2R}\right)\frac{dn}{dz}, \tag{3}$$

where R is the radius of curvature induced by the tension in the wax. Integrating Eq. (3) as before we get

$$v = \frac{1}{3\pi\sqrt{Rt/2}}\,\frac{Dn}{N}. \tag{4}$$

Comparing Eqs. (2) and (4) we see that the effective depth "L" of the channel is fixed at a small value $\pi\sqrt{Rt/2}$, roughly the geometric mean of R and t and independent of the actual depth. Since t is a microscopic quantity representing the thickness of the AlAs release layer and the radius of curvature R is a few centimeters, "L" can be as little as 30 μm even when the channel is one hundred times deeper. Contrary to intuition, the need to transport the reaction products away from the etching zone tells us to make the release layer as thin as possible! We have employed AlAs layers as thin as 20 Å.

The thin films, consisting of layers of GaAs and $Al_xGa_{1-x}As$ ($x < 0.4$) supported by the wax, can be readily handled. We generally make a permanent support by bonding the film to a glass substrate with ultraviolet curable cement of the type used to splice optical fibers. In this way we can make a permanent support for large area crack-free films. After permanent mounting the wax is simply washed away in trichloroethylene. Such films are very durable and easily survive a fingernail test. We have also experimented with direct "optical contacting" to glass substrates (Van der Waals bonding) without the benefit of any adhesive. This bond is also essentially permanent but it requires greater care in establishing adhesion.

We anticipate that the ability to remove large area epitaxial films from reusable growth substrates can open new possibilities for integrating III-V technology with other materials technologies such as silicon wafers, optical fibers, etc. The desire to eliminate the bulk GaAs substrate wafers may be driven by a thermal conductivity problem, a mechanical problem, or simply a cost problem as in solar cells.

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