Vapor phase epitaxial liftoff of GaAs and silicon single crystal films

W. Chang, C.P. Kao, G.A. Pike, J.A. Slone, E. Yablonovitch*

Electrical Engineering Department, University of California, Los Angeles, Los Angeles, CA 90095-1594, USA

Abstract

Among the technologies for integrating GaAs devices with Si VLSI chips, epitaxial liftoff (ELO) is conspicuous for maintaining the quality of the single crystal epitaxial GaAs films. Traditionally, ELO is implemented in aqueous HF solution. It would be cleaner and simpler if ELO could be implemented in a vapor process. In this article, we will present the potential improvements in the ELO process by using a vapor phase etch to undercut thin films. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Vapor phase; Epitaxial liftoff; GaAs; Silicon single crystal films; Hydrofluoric acid

Epitaxial liftoff, the separation and manipulation of thin electronic films removed from their substrates, has taken its place among the semiconductor processing and packaging technologies. It relies upon the extreme chemical selectivity which frequently manifests itself in the wet chemistry of organic, inorganic, and epitaxial materials. In this article we explore the prospects of converting epitaxial liftoff (ELO) into a vapor phase process, VELO, hopefully with attendant process simplification.

There have been a great many tests of the effect of the ELO process on lifted off devices [1]. The outcome of all this testing is that, as a general rule, electronic devices are unharmed by the liftoff process. However, there is some susceptibility to pinholes in the epitaxial films, and in large area devices such as solar cells, there is a significant risk of forming cleavage cracks. These cleavage cracks are open circuits to current flow, and will leave the solar cells open-circuited or at least very resistive.

---

* Corresponding author. E-mail. eliy@ucla.edu.

The normal cleavage planes in III–V semiconductors are $\langle 1\,1\,0 \rangle$ oriented. As free standing thin films, GaAs sheets have very little mechanical strength, and need to be mechanically supported at each stage of the liftoff process. The strength of GaAs is such that a strain as small as 0.1% can produce cleavage cracks.

The mechanical support can be helpful by supplying compressive stress on the thin GaAs films, or it can be harmful by causing the film to stretch. The films are strong in compression, but weak in tension. During the liftoff, some parts of the film are still attached while other parts are already free. The non-uniformity of these effects tends to put undesirable tensile strains on the films during the liftoff process.

It is now generally accepted that cleavage cracks are the main problem in the application of ELO to solar cells. There is some recent work [2] from the Netherlands which addresses some of these problems. They have introduced some significant new innovations.

They cover the GaAs liftoff film with 2–3 μm of evaporated copper metal. This provides both mechanical strength and a favorable thermal expansion co-efficient. Copper contracts more when being cooled from temperatures above ambient, and therefore provides desirable compression on the GaAs film. This allows some tensile stress to be applied during liftoff, which apparently expedites the etch rate. Under cutting rates on the order of 1 mm/h were demonstrated, which is faster than the normal etch rate ≈ 0.3 mm/h. We presume that this might be attributed to stress-enhanced corrosion, which is a well-known effect in metallurgy. A single droplet of HF acid applied to the wafer edge provided the undercut etch in the work by van Geelen et al. [2].

In this article we will present experimental parametric studies on using acid vapor rather than an aqueous acid for implementing the liftoff process. This permits a cleaner liftoff process, with process simplifications that may assist in addressing the cleavage crack issue. A similar vapor ELO process is presented here for both GaAs/AlAs/GaAs epi-wafers, as well as Si/SiO_2 silicon-on-insulator wafers.

There have been a number of previous studies of using HF acid vapor for micro-electro-mechanical micro-fabrication and processing steps [3,4]. In addition there have been studies using anhydrous HF vapor [5]. Here we address the effects of acid vapor partial pressure, and its influence on under cutting speed in comparison to aqueous HF acid.

We have chosen to work with the vapor of concentrated hydrofluoric acid (49%), since it is close to the azeotropic composition, which is where the chemical composition in the vapor matches [6] that in the liquid. A diagram of our undercut etching apparatus is shown in Fig. 1. The typical N_2 vapor flow rates in the 500 ml undercutting chamber were 100 ml/min.

Both GaAs and silicon on SiO_2 (SOI) samples were investigated in this work. The GaAs sample consisted of an N on P $Al_{0.3}Ga_{0.7}As$/GaAs double heterostructure, 1 μm thick on a 50 nm GaAs ELO etch-stop protection layer, over a 100 nm AlAs sacrificial layer on a GaAs buffer layer. The SOI sample consisted of Si and SiO_2 layers with thickness of 330 nm and 150 nm, respectively. All samples were tested under two situations: A rigid backing during liftoff, and a convex undercutting slot during liftoff. The convex films were supported by wax. As they were undercut the
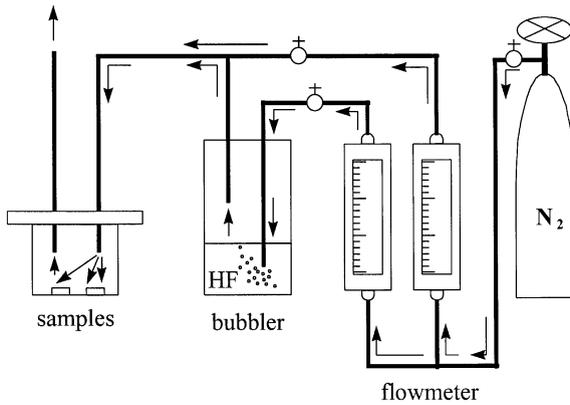
Fig. 1. Experimental setup for vapor ELO. The symbols ⚵ represent flow control valves which blend the saturated vapor from the bubbler with dry N_2 to adjust the acid vapor pressure.

tensile stress in the wax would be relieved by inducing a curvature on the semiconductor film, making the etching slot convex. The rigid backing consisted of a silicon chip on a wax adhesive film 1 or 2 μm thick. Under these circumstances the etching slot remained parallel. The etch depth was determined by using adhesive tape to pull off the undercut portion of the films.

We plot the lateral under cutting rates versus the percentage of saturated vapor, a kind of relative humidity for the acid vapor. One hundred percent of saturation could lead to condensation. Less than 100% of saturation is dry in principle, but the condensation conditions could be quite different in a narrow slot where surface energies influence the condensation equilibrium. Furthermore, since the acid reacts with the AlAs or SiO_2 surface, the reaction products may have a smaller vapor pressure and remain condensed. Therefore the process cannot be regarded as completely dry, even when the vapor pressure is $< 100\%$ of saturation. We can assume that sub-microscopic amounts of aqueous acid may be present in the etching slot. In addition, the mass transport conditions might be different in gas phase vapor etching than in aqueous bath etching.

Fig. 2a shows the initial etch rate of 50 nm thick AlAs slots. (All the initial etch rates were measured after 1 h in the etchant.) The vapor etch rate is noticeably slower than the aqueous solution point marked on the right-hand axis. The scatter is due to non-uniformity in the etch rate. The etch rate is maximum at saturation, but unsaturated vapors were almost equally effective. These etch rates are all slower than the stress-induced etch speedup measured by van Geelen et al. [2]. Stress is a double edged sword, and we were trying to avoid the risk of cleavage crack formation.

In Fig. 2b the cumulative etch rate, after 12 h is given. Generally the etching slows down in a deeper slot owing to the difficulty of mass transport of reactants and reaction products into and out of the slot. One must assume that the similarity between the aqueous result and the 100% saturation vapor pressure result for the convex slot in Fig. 2b is related to the condensation of microscopic amounts of
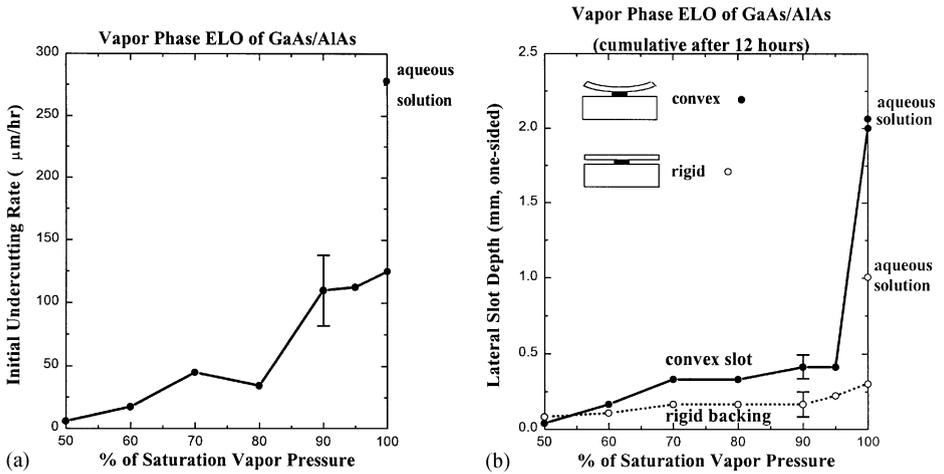
Fig. 2. (a) Initial lateral under cutting rates versus the percentage of saturated vapor pressure for GaAs wafers. The aqueous points on the right-hand axis represent the corresponding rate for 10% HF aqueous acid. (b) Cumulative lateral under cutting distance after 12 h versus the percentage of saturated vapor pressure, for GaAs wafers. The aqueous points on the right-hand axis represent the corresponding distance for 10% HF aqueous acid.

aqueous acid in the slot. Mass transport is somewhat easier in the convex geometry as originally discussed in Ref. [7]. Nonetheless, even the plane parallel slot labeled as rigid, allows a 2 mm wide stripe to be undercut in 12 h in aqueous acid. This is surprisingly good in view of the mass transport issues. A large area array consisting of 2 mm stripes would be ideal for solar cells, since the stripes would be amenable to series connection, producing a high voltage, and solving one of the packaging problems in solar panels. As mentioned earlier, however, the problem is to prevent cracking in such stripe arrays.

We have also performed vapor ELO measurements on SOI films, as shown in Fig. 3a. The initial vapor undercutting rate is slightly slower than in aqueous solution. However the cumulative rate in aqueous etch comes to a halt at about a 500 μm slot depth, to be contrasted with the vapor etch which continues to etch almost linearly with time and does not slow down. The mass transport issues for SiO_2 slots are analyzed in Ref. [8]. The high solubility of the SiF_4 reaction products should permit the aqueous etching to continue with little slowdown in slots deeper than 500 μm. Therefore the halting of the cumulative aqueous etching in Fig. 3b is puzzling to us, but gratifyingly the vapor etch seems to not have that problem. Again arrays of 2 mm wide stripes should be available from SOI wafers. If these could be manufactured, and the substrates re-used, at low cost, then this would also be a possible thin film solar cell option.

We have demonstrated that HF acid vapor ELO is a viable option for separating thin film solar cell material from a parent substrate and is comparable or superior to aqueous acid liftoff. As in all ELO, the separated substrate is in excellent
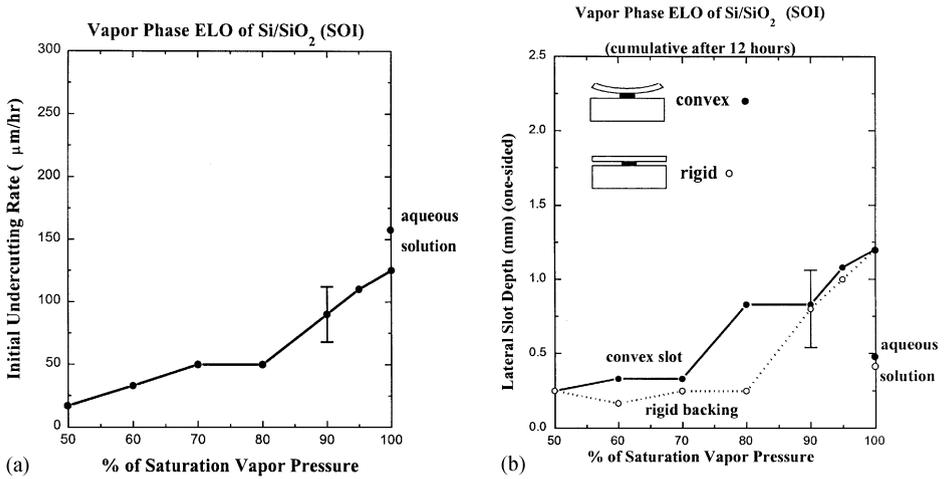
Fig. 3. (a) Initial lateral under cutting rates versus the percentage of saturated vapor pressure for SOI wafers. The aqueous points on the right-hand axis represent the corresponding rate for 49% HF aqueous acid. (b) Cumulative lateral under cutting distance after 12 h versus the percentage of saturated vapor pressure for SOI wafers. The aqueous points on the right-hand axis represent the corresponding distance for 49% HF aqueous acid.

condition and ready to be re-used. The vapor process is essentially dry, except that sub-microscopic amounts of liquid acid might actually be present inside the under cutting slots.

Large areas of ELO films will be needed for producing significant amounts of photo-voltaic energy. The major problem in the ELO process as applied to solar cells is the scale-up to large area crack-free sheets. Indeed large sheets of many small discrete devices do not present insurmountable ELO problems and large arrays of 1 or 2 mm stripes can be lifted off. But in large area devices such as solar cells, the failure mode turns out to be the risk of cleavage cracks being formed in the lifted off thin films. Crack formation is a stubborn issue that may require new approaches such as those introduced by the Netherlands group [2].

References

[1] W.K. Chan, E. Yablonovitch, in: M. Dagenais, R.F. Leheny, J. Crow (Eds.), Integrated Optoelectronics, Academic Press, New York, 1995, p. 297.
[2] A. van Geelen, P.R. Hageman, G.J. Bauhuis, P.C. van Rijsingen, P. Schmidt, L.J. Giling, Mater. Sci. Eng. B 45 (1997) 162.
[3] T.A. Lober, R.T. Howe, in Technical Digest of IEEE Solid-State Sensor and Actuator Workshop, TH0215-4, 1988.

[4] K.R. Williams, R.S. Muller, J. Microelec.-Mech. Systems, 5 (1996) 256.

[5] Y.I. Lee, K.H. Park, J. Lee, C.S. Lee, H.J. Yoo, C.J. Kim, J. Microelec.-Mech. Systems, 6 (1997) 226.

[6] R.A. Smith, in: M. Howe-Grant (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., vol. 11, Wiley, New York, 1991, p. 361.

[7] E. Yablonovitch, T.J. Gmitter, J.P. Harbison, R. Bhat, App. Phys. Lett. 51 (1987) 2222.

[8] D.J. Monk, D.S. Soane, R.T. Howe, J. Electrochem. Soc. 141 (1994) 270.