Van der Waals bonding of GaAs epitaxial liftoff films onto arbitrary substrates

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Epitaxial liftoff is an alternative to lattice-mismatched heteroepitaxial growth. Multilayer $Al_xGa_{1-x}As$ epitaxial films are separated from their growth substrates by undercutting an AlAs release layer in HF acid (selectivity $\gtrsim 10^8$ for $x \leqslant 0.4$). The resulting $Al_xGa_{1-x}As$ films tend to bond by natural intermolecular surface forces to any smooth substrate (Van der Waals bonding). We have demonstrated GaAs thin-film bonding by surface tension forces onto Si, glass, sapphire, $LiNbO_3$, InP, and diamond substrates, as well as self-bonding onto GaAs substrates. In transmission electron microscopy the substrate and thin-film atomic lattices can be simultaneously imaged, showing only a thin (20–100 Å) amorphous layer in between.

In the field of electronic materials there has been a persistent interest in the integration of epitaxial quality, single crystalline, thin-film semiconductor layers with arbitrary substrates. This has led to a massive effort[1] on lattice mismatched heteroepitaxial growth. Recently, however, a new and more flexible approach[2] has been attracting increasing attention.

In this new approach, perfect epitaxial $Al_xGa_{1-x}As$ thin films are lifted off lattice-matched GaAs growth substrates by means of an ultrathin AlAs release layer. We take advantage of the extremely selective etching ($\gtrsim 10^8$) of AlAs in dilute hydrofluoric acid. Crack-free epitaxial films as large as 2 cm×4 cm and as thin as 200 Å have been lifted off in this way. The GaAs substrate is left intact and can be reused if so desired, while the epitaxial thin film can be cemented or alternatively "Van der Waals" bonded by surface tension forces to any arbitrary substrate.

To date a number of devices have been demonstrated: double-heterostructure GaAs/AlGaAs thin-film diode lasers on glass,[3] GaAs light-emitting diodes on silicon,[4] GaAs metal-semiconductor field-effect transistors (MESFETs) on glass and silicon,[5] strained single quantum well InGaAs/GaAs high electron mobility transistors (HEMTs) on glass and silicon,[6] and GaAs optical receivers integrated onto $LiNbO_3$ waveguides.[7]

We have recently extended this technological approach to InP-based semiconductors (e.g., quarternaries) through the use of ultrathin (< 50 Å) pseudomorphic strained AlAs release layers. A high-speed quarternary photodiode was lifted off InP and integrated[8] onto a sapphire substrate.

In handling such epitaxial films after liftoff, one notices a peculiar adhesion property. They tend to adhere to any smooth surface. The flexibility of the supported film allows it to conform to the undulations of a smooth substrate. This frequently results in a type of "optical contacting" or intimate interfacial contact between the epitaxial film and a new substrate. Surface forces tend to form a permanent bond without the need for any adhesives. We have called[2] this "Van der Waals" (VDW) bonding due to the presumed role of interfacial forces.

Numerous advantages accrue if the film-substrate bonding can be achieved without the explicit need for adhesives:

(1) Thermal processing of the bonded films is permissible at normal semiconductor processing temperatures, rather than the more modest temperatures which most adhesives could tolerate. Indeed we have cycled[9] a GaAs film VDW bonded onto a silicon substrate back up to 750 °C, organometallic chemical vapor deposition growth temperature, for the regrowth of quantum wells.

(2) Very close contact between the film and substrate is necessary for good thermal conduction. For example, we have VDW bonded GaAs epitaxial liftoff films directly to diamond substrates which could act as very effective heat sinks.

(3) Optical coupling between a semiconducting film detector and a substrate waveguide[7] requires a very intimate contact for good coupling efficiency.

(4) For highly doped semiconductors, an Ohmic contact between film and substrate may be possible if the tunnel barrier is thin enough to allow electrical conduction. This would lead to a type of three-dimensional vertically integrated device structure.

Therefore, we are amply motivated to find improvements in the VDW bonding process and to learn some of its limitations.

We now outline the VDW bonding processing steps as practiced in our laboratory. The critical role is played by the wax-like material which is applied to the epitaxial film prior to liftoff and which will support the film after liftoff. We employ a proprietary mixture of hydrocarbons known as Apiezon W. We first apply the wax by melting a pellet onto the epitaxial film in an oven at 125 °C, a temperature at which the viscosity remains high enough to prevent the wax from flowing uncontrollably. Then the melted wax pellet is flattened to a uniform thickness at 75 °C by means of a Teflon press. This temperature is low enough that the Teflon will not stick to the wax, but high enough to allow the elastic stresses in the wax to anneal out. To further this end, the wax might be annealed as described in Ref. 2, producing a slightly domed top surface. At this point the supporting wax is a plane parallel layer, 0.1 to 0.5 mm thick, but slightly domed.

Now it is necessary to uncover the edges of the buried AlAs layer (typically 500 Å thick) so that the HF acid can etch it away. We have used three different methods:

(1) The AlAs layer around the edges of the wax can be exposed by using a nonselective etch, with the wax itself acting as a mask.

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(2) The edges can be exposed by cleavage after the face of the semiconductor wafer has been coated with wax.
(3) After the top surface of a wafer chip is covered with wax, the edges can be exposed by simple edge grinding.

We undercut the epitaxial liftoff film in a 10% aqueous dilution of HF acid in a sealed beaker at 0 °C. The etch rate of undercutting is ~0.3 mm/h for epitaxial film stripes narrower than 1 cm. (A rectangular film shape is better than a square shape since it helps to establish the required axis of curvature. There is no apparent limitation on stripe length.) For stripes between 1 and 2 cm in width the etch rate goes down, apparently due to insufficient curvature[2] induced by the wax. We have not undercut stripes wider than 2 cm.

Once the undercutting is complete, the film can be picked up and manipulated by a vacuum tool. It is usually then rinsed in de-ionized water. Afterward, it is best not to dry the film completely. A tiny water droplet should be left behind, since the surface tension of the water will play a critical role in the VDW bonding. Using the vacuum manipulator tool, the film is accurately positioned on the substrate. As long as the mean wetting angle[10] on the thin film and substrate surfaces is $<90°$, the effect of the water's surface tension will be to pull the film down onto the substrate. This is the initial step in bonding by natural intermolecular surface forces.

At this point an excess of water remains trapped between film and substrate. The next step is illustrated in Fig. 1. Pressure is applied to the film to squeeze out the water. Typically, as an upper limit, we use no more than a pressure $p = 1.5\times 10^4$ dynes per square millimeter. On a transparent substrate we can see from beneath that the remaining water produces only one Newton's ring or optical fringe, implying ≈ 1000 Å thickness of water. Indeed, the capillary pressure of a water film, few thousand angstroms thick, is able to balance such a pressure p.

To blot up the excess water which has been squeezed out around the edges of the film, the pressure is sometimes applied by means of a pad of clean room tissues. It is necesary for the wax to be slightly domed so that the pressure is greater in the middle of the film than at the edges. Once the excess is removed, the remaining water, as represented by the single optical fringe, disappears over a period of several hours! Apparently surface tension forces pull the water out to the edge of the film as it evaporates. The narrow diffusion path is seemingly adequate, since the volume which needs to diffuse out is exceptionally tiny.

The VDW process seems to rely on a favorable inequality of surface-free energies: If the substrate-film interfacial energy γ_{sf} is less than the sum of water-substrate γ_{ws} and water-film γ_{wf} surface energies, then the water will tend to be forced out as the film and substrate surfaces coalesce together.

$$\gamma_{sf} < \gamma_{ws} + \gamma_{wf}. \quad (1)$$

The wax is then rinsed away in trichloroethylene leaving a semiconductor film VDW bonded to a substrate. An example of a semitransparent VDW bonded GaAs film, 1500 Å thick, on a glass substrate is shown in Fig. 2. Under an optical microscope there is no apparent remaining water, except around dust particles which had been trapped between film and substrate. (Our work was carried out in a normal laboratory environment rather than special clean room surroundings.) The dust particles appear to raise tiny tent-like structures under the thin film. The tent-like structures are easily seen in the optical microscope since they cause a series of miniature Newton's rings around each dust particle. Subjected to flash heating, these hydrated dust particles can produce blisters under the film. Therefore, if the film is to further processed at temperatures in excess of 250 °C, it is

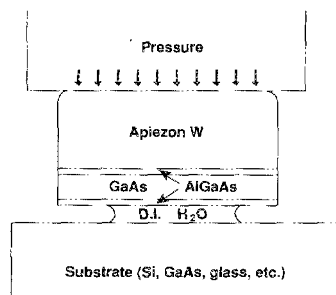

FIG. 1. In the "Van der Waals" bonding process a thin epitaxial film is married to a foreign substrate: After epitaxial liftoff by selective etching, the film is supported by Apiezon W, a wax-like material. The surface tension of de-ionized water acts initially to pull the film down onto the substrate. Then pressure must be applied to remove all but one optical fringe thickness of water. The remaining trace of water seems to evaporate, leaving a permanent bond between film and substrate.

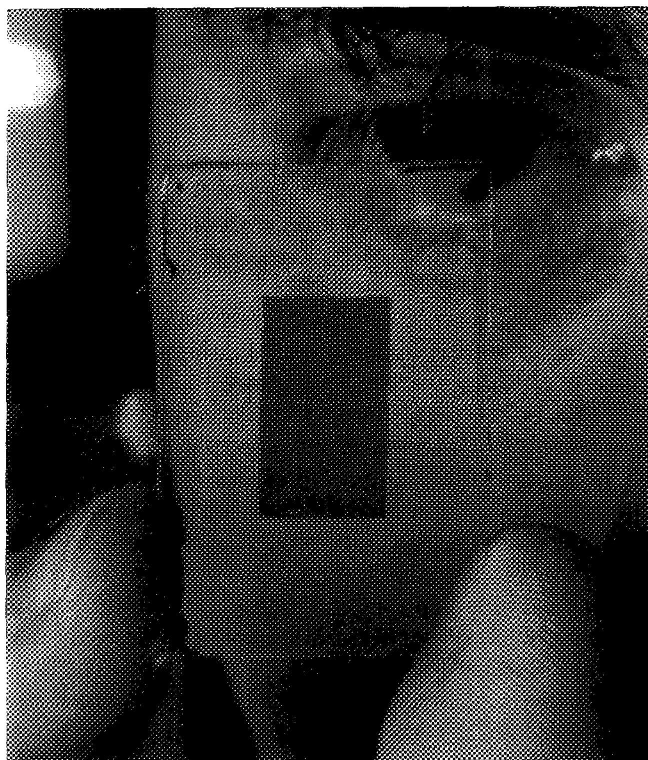

FIG. 2. Semitransparent VDW bonded film, an $Al_{0.3}Ga_{0.7}As/GaAs/Al_{0.3}Ga_{0.7}As$ double heterostructure, 1500 Å thick, on a glass substrate.

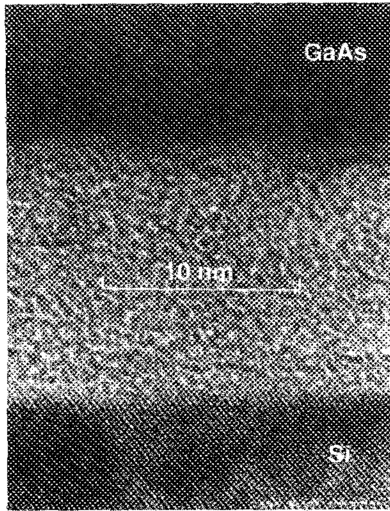

FIG. 3. Cross-sectional transmission electron micrograph of the "Van der Waals" bond between a GaAs film and a silicon substrate. By manually aligning the crystallographic axes during the bonding process, simultaneous lattice imaging of film and substrate is evident. Notice the difference in lattice constant. The amorphous interlayer, ≈ 100 Å thick, appears to consist of silicon oxides.

given a long, slow, vacuum bake[9] in an attempt to dehydrate the dust particles. Except for these dust particle defects, the film-substrate interface is optically featureless.

To determine the nature of the VDW bond, we embarked upon a program of cross-sectional transmission electron microscopy (TEM) of the interfacial region between film and substrate. GaAs films were bonded to a variety of substrates, including silicon, GaAs, and $LiNbO_3$. Then they were sectioned by standard TEM sample preparation techniques. During the VDW bonding step, some care was taken in the manual alignment of cyrstallographic axes between film and substrate. By manually aligning the crystal orientations to within about $\sim 0.5°$, a simultaneous lattice image of the film and underlying substrate was made possible. Such a TEM micrograph is displayed in Fig. 3 for the case of GaAs films on silicon substrates. The difference in lattice constant between the GaAs and silicon is immediately apparent. The main point of the micrograph is the amorphous interlayer, ≈ 100 Å thick, which acts as the bonding layer.

A similar micrograph for the case of GaAs films on GaAs substrates is shown in Fig. 4. In this case the amorphous bonding layer averages only ≈ 20 Å in thickness. There are very noticeable surface undulations, particularly on the chemically etched substrate. The interfacial amorphous regions seems to accommodate the surface undulations and fill them in, so that its actual thickness varies anywhere from 0 to 40 Å. A point of direct "touching" between film and substrate can actually be seen in Fig. 4.

The amorphous interlayers in Figs. 3 and 4 appear to consist of semiconductor surface oxides. Energy dispersive x-ray fluorescence analysis indicated that no more than a monolayer of elements with atomic number > 11, other than the semiconductor elements themselves, was present in the amorphous interlayers. The amorphous interlayer on silicon substrates was thicker (100 Å) than on GaAs substrates (20 Å). Since the native oxide on silicon is not normally expected to exceed 30 Å in thickness, we may guess that the electrochemical couple between the dissimilar film and substrate

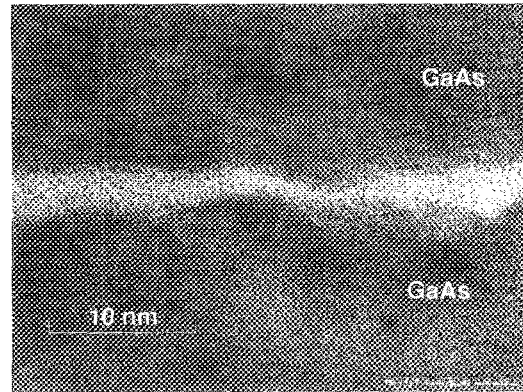

FIG. 4. Cross-sectional transmission electron micrograph of the "Van der Waals" bond between a GaAs film at the top and a GaAs substrate below. Again simultaneous lattice imaging is made possible by manual alignment prior to bonding. In this case the amorphous interlayer averages ≈ 20 Å thickness, most of which seems to be due to inherent substrate roughness. Notice the apparent point of "touching" in the right center of the micrograph.

may have induced the extra oxide growth. This suggests that the thicker interlayer on the silicon substrate was predominantly an oxidized form of silicon.

To influence the oxide thickness we have used liquids other than de-ionized water to provide the initial surface tension for the VDW bond. In particular, $(NH_4)_2S$ aqueous solutions have been shown[11] to be very effective in cleaning native oxides off GaAs surfaces. This had no effect on either the GaAs/GaAs amorphous interlayer thickness or the GaAs/Si interlayer thickness. The $(NH_4)_2S$ aqueous solutions were quite helpful, however, in establishing a mean wetting angle $< 90°$ to allow GaAs VDW bonding onto diamond substrates.

We have also measured the interlayer thickness for GaAs VDW bonding on $LiNbO_3$ waveguide[7] structures. The amorphous layer thickness was ≈ 100 Å, which is thin enough to provide good optical coupling.

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