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Selective Oxidation Technology and its Applications toward Electronic and Optoelectronic Devices

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Abstract

Selective oxidation of AlGaAs compounds has facilitated dramatic improvements in the performance of near IR VCSELs. Under the auspices of this proposal we have: (1) expanded our understanding of both the strengths and the limitations of this technology; (2) explored its applicability to other Al bearing materials; (3) utilized this technology base to demonstrate a variety of new electronic and optoelectronic devices; and (4) established the reliability and manufacturability of oxidized devices such as VCSELs. Specifically, we have investigated conditions required to maximize control of the oxidation process as well as those required to facilitate/inhibit etching of the resultant oxide. Concurrently, studies were performed to extend the technology to other Al-bearing compounds such as Al(Ga)AsSb, InAl(Ga)P and Al(Ga)N. Several new devices utilizing the selective oxidation technology of AlGaAs, as well as Al(Ga)AsSb were be considered. On a separate front, we also explored the possibility of using oxidized AlGaAs and InAl(Ga)P to form GaAs/AlGaAs FETs. Finally, reliability and manufacturability issues of the high performance VCSELs fabricated using selective oxidation technology, were addressed.

Contents

1. Introduction
2. Oxidation of AlGaAs
3. Oxidation of AlGaAs for VCSEL and waveguides
4. Oxidation of AlGaAs for MISFET applications
5. Oxidation of other Al-bearing III-V materials
6. Conclusion

I. Introduction

This LDRD project was directed toward study of the selective, steam oxidation process of Al-bearing III-V compounds, most significantly AlGaAs grown on GaAs. We have extracted temperature, time and Al mole fraction dependence of this process, as well as noted dependence on other variables such as layer thickness, carrier gas, adjacent layer thickness and others. We have applied this knowledge to engineer VCSELs that utilize the oxidized layer as a current constriction. We have obtained excellent results in terms of threshold current and wall plug efficiency of these devices. Finally, reliability and manufacturability issues of the high performance VCSELs fabricated using selective oxidation technology, was addressed

In addition, layers of oxidized AlGaAs were investigated as a means of forming various optical elements, such as convex and concave lenses that could be embedded into an assortment of surface normal, multilayer devices. Oxidized AlGaAs was also investigated for integration into waveguides, in particular as a means of inducing very large form birefringence. We have investigated the utility of application of to MOSFET devices and discovered some limitations of the oxidation process, which may limit its use for this type of application.

Furthermore, other III-V compounds, which contain Al, have been studied as candidates for oxidation. In particular, we have oxidized AlGaAsSb on InP substrates and noted a novel and distinct oxidation process, which resulted in formation of the Al-oxide as well as a semi-metallic Sb layer.

II. Oxidation of AlGaAs

In the recent years, there has been a great deal activity in the area of oxidation of Al-bearing III-V compounds, especially AlGaAs. Unlike Si, GaAs is not known to form stable oxides, such as SiO₂. The fact that Si forms a stable, uniform oxide is of great technological importance in the area of microfabrication. Similarly, the fact that oxides of GaAs are unstable (and poisonous) is one of the limitations of this material system in the area of microfabrication, especially microelectronics. However, GaAs is extensively used for optoelectronics and many have noticed reliability problems of devices due to a particular degradation of high Al mole fraction AlGaAs and formation of a native (gibbsite phase) oxide. Of course it was a highly undesirable phenomenon that needed to be understood in order to be corrected. Thus several workers set out to duplicate and speed up the natural degradation of AlGaAs in atmospheric conditions in order to understand it as far back as 1979. Then in 1990, a group from University of Illinois found that by exposing high Al mole fraction AlGaAs to a wet steam environment at elevated temperatures (~400°C) resulted in formation of a new type of Al-oxide. This oxide was different from the type that forms naturally when AlGaAs is exposed to atmospheric conditions. It was chemically and mechanically stable, and thus useful in device fabrication. Other differences between the natural, atmospheric (gibbsite) oxide and the “steam” oxide include formation at an elevated temperature (near 400°C instead of room temperature), growth within minutes or hours rather than over a period of months and years and contraction rather than expansion upon formation. Finally, the “steam” oxide exhibits a low refractive index, on the order of 1.55.

To perform oxidation, first the layers to be oxidized must be exposed to the oxidation atmosphere. If this is to be a surface oxidation (i.e. proceeding perpendicular to the sample surface), no pre-processing is necessary assuming the top most layer is the one to be oxidized. If lateral oxidation is desired (i.e. proceeding parallel to the sample surface), mesas of the material must be etched, such that the sidewalls of layers to be oxidized are exposed. Then samples are put into an oxidation oven. The oxidation apparatus including the oven is shown in Figure 1. It consists of a tube furnace through which hot water vapor is carried by a carrier gas (usually N₂). The furnace and the water bath are temperature controlled to ensure repeatability and consistency of the process.

Figure 1. Oxidation apparatus

The chemical reaction consistent with the formation of the “steam” oxide can be written expressed as follows:

Where ΔG^{698} refers to the Gibbs free energy at a temperature of 698 Kelvin. A negative free energy implies that the process is thermodynamically favored to occur and it should be noted that reactions described in equation (1)-(3) all have negative free energies at temperatures employed. Some noteworthy features of the above reactions include intermediate formation of As₂O₃ and As. Raman studies indicate a relatively constant As Raman signal during oxidation, implying a balance between chemical reaction forming As (equations (2) and (3)) and loss of As. It is thought that As forms AsH₃ with atomic hydrogen ($\Delta G^{698} = -471 \text{ kJ/mol}$), however As itself is sufficiently volatile to remove itself from the oxide. However, the mechanism for removal of As from the oxide is not strong enough to remove all the As, since elemental As is found in or around the oxidized regions. This has grave consequences for the application of these oxides in the MOS area.

Transmission electron microscope (TEM) studies of the oxide confirm that the oxide is a γ -phase Al_2O_3 , although crystallization from the amorphous state maybe brought on by annealing or electron beam of the TEM.

Another interesting feature of the reaction chemistry is that replacement of AlAs by GaAs in equation (1) results in $\Delta G^{698} = +10 \text{ kJ/mol}$, making it thermodynamically unfavorable. Thus one can expect that addition of even a minute amount of Ga to AlAs (to form a high Al mole fraction AlGaAs) greatly slows down the oxidation rate.

Figure 2 Oxidation rate of AlGaAs as a function of Al mole fraction. Indeed, as shown in Figure 2, the oxidation rate of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of x drops precipitously as mole fraction of Al decreases from 1. This property forms a basis for selective, lateral oxidation process, where by slight variation of the Al mole fraction in AlGaAs, chosen layers may oxidize to a desired depth, whereas others do not oxidize much at all. In the regime of interest, the oxidation process proceeds with linear rates and no induction period and exhibits Arrhenius temperature dependence (see Figure 3).

Figure 3 Oxide length as a function of oxidation time for 1.0 and 0.98 Al mole fraction and two different oxidation temperatures (400°C and 440°C).

This regime assumes operation in a water vapor saturated regime, assuring that the reaction rates are not reactant limited. In our 4-inch diameter oven, a 3-l/min flow of N_2 allows operation in that region. While most common carrier gas is N_2 , other gasses have been studied as well. Curiously, while there isn't much difference between N_2 , Ar or 3% H_2 in N_2 , use of O_2 as a carrier gas quenches oxidation completely. This most likely is related to the crucial role of hydrogen in removal of As from the oxide.

In addition to the strong dependence on temperature and Al mole fraction, the oxidation rate depends on the thickness of the layer to be oxidized, once that thickness drops below 80 nm. This thickness dependence has been ascribed to Gibbs-Thomson effect, whereby the interfaces of the layers surrounding the oxidized layer exert pressure opposing formation of the new oxide. This results in a greater curvature of the oxidation terminus and slower oxidation rates in thin oxide layers. This property can also be used to an advantage in device fabrication by choosing appropriate layer thickness to control the extent of oxidation. Finally, it has been found that the oxidation rate can also be controlled by the thickness of the layers adjacent to the oxidized layer.

Figure 4 Cross sectional SEM of a partially oxidized sample, showing the influence of the thickness of GaAs barriers on the oxidation rate of the adjacent AlGaAs with 0.94 Al mole fraction

Figure 4 shows a structure where 94% and 98% Al containing AlGaAs layers are separated by different thickness GaAs layers. While 98% Al AlGaAs layers of the same thickness all oxidized to approximately same extent, the 94% layers oxidized further if they are separated from the 98% layers by thinner rather than thicker GaAs layers. This phenomenon is a result of the diffusion of the oxidant through a GaAs barrier to aid in the oxidation of the slower oxidizing AlGaAs layer, where the faster oxidizing AlGaAs layers serve as a feeder channel. Oxidation is a two-dimensional process, with the oxide forming in a lateral as well as transverse direction. By retarding oxidation in the transverse direction (with the use of low Al containing barriers) oxidation fronts of an arbitrary shape can be obtained. This property has been put to a use in fabrication of buried optical elements such as lenses.

III. Oxidation of AlGaAs for VCSELs and waveguides

Optical properties of the oxides formed by steam oxidation of interest owing to their growing applications not just as an insulator, but as a low refractive index dielectric. One of the most important characteristics is the refractive index, which has been measured to be near 1.55. Another property of interest is the optical loss of the oxidized layers. While this is not particularly crucial in VCSELs, since the radiation propagates perpendicular to a small thickness of an oxide, it is of great interest in waveguide applications.

Transmission of the oxide layers has been characterized in the near infrared and infrared region has been measured. It shows a clear dip in transmission near 3 μm , which is associated with absorption due to OH groups in the oxide. Beyond that wavelength, Al-oxide appears to be fairly transparent out to 8-9 μm .

The infrared absorption of oxides is important in applications where oxide layers are used in nonlinear waveguide for difference frequency generation. Because of the large differential in the refractive index of the oxidized AlGaAs and un-oxidized AlGaAs or GaAs, it is possible to induce a very large form birefringence in waveguides. This in turn allows a true phase match to occur for pump, signal and idler wavelengths, resulting in an appreciable efficiency of difference frequency generation. However, the issue of propagation losses in such oxidized waveguides remains important. We have fabricated some oxidized waveguides designed to phase match light at 950 nm, 1320 nm and 3450 nm. Figure 5 shows a SEM of a partially oxidized waveguide cross section.

Figure 1. Cross sectional scanning electron microscope view of the partially oxidized waveguide. Dark areas are oxidized.

Losses in the unoxidized guides have been measured at 6-7 dB/cm, while oxidized guides exhibit losses near 2-3 dB/cm. This is still somewhat high, but an encouraging result. The most common use of oxides in the waveguide devices, involves current confinement in EELs. In fact, the first devices utilizing the oxidized layers were EELs, where oxide acted to confine the current to the active region as well as provide an index guide. However, the most spectacular improvements in performance were brought about by application of oxides to VCSELs. Again, the oxidized layers were employed to provide current confinement, as shown in Figure 5.

Figure 5 Schematic drawing of the current apertures formed by the oxidized layers in a VCSEL

Also, the thin oxide layer (aperture) placed next to the active region decreased optical losses, providing a measure of lateral confinement due to its low refractive index. This resulted in shrinkage of the active volume and loss reduction and thus a great reduction in the threshold current (breaking the 1 mA barrier). By appropriately tailoring the Al mole fraction of the layer to be oxidized, it is possible to oxidize only the confinement layers, without affecting the DBR layers or the active region. Thus a buried, dielectric aperture may be formed. By refining these concepts, VCSELs with oxide aperture soon demonstrated record high efficiency and low voltages in addition to low threshold currents, as shown in Figure 6.

Figure 6 Power and voltage as function of injection current in an oxidized VCSEL

As mentioned previously, the ability to tailor the oxidation front by Al-mole fraction, thickness or barrier layer thickness variations has also been applied in devices. The use of tapered oxide apertures in VCSELs has lowered scattering loss even further. Furthermore, buried optical elements such as lenses have also been fabricated using this method. Figure 7 shows a scanning electron micrograph of a cross section of such a buried lens.

Figure 7 Cross sectional SEM of a lens formed by selective, lateral oxidation of AlGaAs

IV. Oxidation of AlGaAs for MISFET

Finally, oxides have been used in the electronic devices, as patterned by the Si devices. Figure 8 shows a schematic of a MISFET structure with a steam-oxide gate insulator. However the problem of As segregation and incomplete removal from the oxide results in interfacial state formation, which severely limits usefulness of the Al-oxides for this type of electronic applications. The presence of interfacial As and defects associated with its presence can also have a negative effect on optical properties of nearby quantum wells, thus positioning of the active region at least 20 nm from the oxidized layers is crucial .

Figure 8 Schematic drawing of a MISFET with wet-oxide gate insulator

We have modeled how the production of large amounts of elemental As during the oxidation and its diffusion into adjacent regions can modify the properties of these regions in ways that impact device design, fabrication, and performance. The oxidation rate is determined primarily by the Al mole fraction, but the close proximity of a faster-oxidizing layer can produce a several-fold increase in oxidation rate for a layer of a given Al composition over the rate obtained with an isolated layer of the same composition. Injection of As interstitials into adjacent layers and the resulting development of defects, such as As antisite defects and group-III vacancies and interstitials, can alter the oxidation rate for nearby regions. Observed rate accelerations are consistent with the diffusion of As-generated defects from the fast-reaction layer to the slower-reaction layer. Our model based on the role of elemental As in such behavior as enhanced oxidation rates in close proximity to faster-oxidizing layers, the effect of relative layer thicknesses, and dependence of oxidation rate on position within the total structure provides a semi-quantitative prediction of oxidation profile for complex structures.

During the third year of the LDRD program, an alternative strategy for reducing the interface state density of insulator-GaAs interfaces was explored. A sulfur-based wet chemical surface passivation treatment was applied to freshly etched GaAs surfaces prior to formation of the insulator layer. Early testing involved the use of a low temperature deposited insulator, silicon oxynitride, which was chosen in order to reduce the possibility of sulfur migration from the interface during insulator formation. Electrical measurements of metal-insulator-S-passivated GaAs structures revealed a strong

electrical influence of the sulfur at the interface, however, it was not possible to deduce the amount of interface state reduction, due to the poor electrical properties of silicon oxynitride layers, which are known to have high defect trap densities.

V. Oxidation of other Al-bearing III-V materials

In addition to AlGaAs, other Al-bearing III-V compounds have been oxidized. For example, oxidation of AlAsSb has been demonstrated. Composition resulting in the lattice match to InP contains a Al mole fraction of 1, since this material has a mixed column V composition (As and Sb) and only one column III constituent. While even more readily oxidized than AlAs, this material forms Al-oxide (like AlAs) as well as an interfacial layer of semi-metallic Sb. One could say that upon oxidation this semiconductor decomposes into a dielectric and a metal! It should be noted that the Sb layer does in fact exhibit a greatly reduced resistance as compared to an un-oxidized structure, as shown in Figure 9.

Figure 9 Transmission line measurements showing greatly reduced resistivity of an oxidized structure compared to an unoxidized structure

Figure 10 shows a cross sectional SEM of a partially and fully oxidized AlAsSb layer. Curiously, as the mole fraction of As is varied from 0 (AlSb) to 1 (AlAs), oxidation depth of AlAsSb varies dramatically (Figure 11). Largest depths are observed for As mole fractions corresponding to lattice match to InAs and GaSb substrates. These depths and the one for the composition resulting in lattice match to InP are quite a bit larger than the AlAs oxidation depth. However in absence of any As (AlSb), no oxidation at all is observed. Yet exposure to the steam environment at an elevated temperature, clearly

alters the exposed side wall surface of AlSb, since no atmospheric oxidation occurs afterwards.

Figure 10 Cross sectional SEM of partially and fully oxidized AlAsSb layers. The dark areas are oxidized.

Figure 11 Oxidation depth as a function of As mole fraction for oxidation at 380 °C for 20 minutes

VI. Conclusion

The area of oxidation of Al-bearing III-V compounds has experienced a great deal of growth in the past years. It has been shown to be a powerful concept in fabrication of optoelectronic devices in general and especially VCSELs. It has also been applied to waveguides and electronic devices such as MISFETs. Materials other AlGaAs are suitable for oxidation, although not necessarily with the same results. Problems associated with As precipitates await further investigation, since their presence limits utility of oxides in electronic applications.

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