# Surface Passivation of New Channel Materials Utilizing Hydrogen Peroxide and Hydrazine Gas

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**Abstract.** In situ gas phase passivation methods can enable new channel materials. Toward this end pure anhydrous HOOH and H2NNH2 membrane gas delivery methods were developed. Implementation led to Si-OH passivation of InGaAs(001) at 350C and Si-N-H passivation of SiGe(110) at 285C. XPS and initial electrical characterization has been carried out. Feasibility for in situ dry surface preparation and passivation was demonstrated.

## Introduction

New in situ gas phase passivation methods can enable new channel materials that will allow better carrier confinement and mobility. These new methods will ideally provide one to three mono-layers of passivation material on multiple types of surfaces and crystallographic faces: $InGa_{1-x}As$, $In_xGa_{1-x}Sb$, $In_xGa_{1-x}N$, SiGe, and Ge. Si-OH and Si-N-H are leading passivation candidates, as they can provide barrier properties preventing metal migration as well as functionalization for subsequent deposition of High $k$ materials. Our approach involves the use of a novel oxidant, anhydrous hydrogen peroxide HOOH(g) or a nitriding agent, in this case hydrazine $H_2NNH_2(g)$, to create terminating Si-OH or Si-NH layers available for additional functionalization.

## Challenges

Though theoretically appealing, an early problem encountered in this approach was the lack of vaporization sources for pure anhydrous HOOH and $H_2NNH_2$ gases. Hydrogen peroxide (HOOH)/Water ($H_2O$) mixtures in liquid form are generally used in semiconductor manufacturing for cleaning and surface preparation. Thirty percent and fifty percent two-component liquid sources for gas phase mixtures have been investigated in a few studies with moderate success [1,2]. Especially noteworthy are Kummel's findings that the use of hydrogen peroxide leads to a 3x increase in oxygen surface density on Ge versus water [3].

## Membrane Technology

In practice $H_2O_2/H_2O$ mixtures have found limited utility in the gas phase due to process problems attributed to the presence of water. Ideally anhydrous hydrogen peroxide liquid would be used as the source, however it is highly unstable and potentially explosive due to its propensity to decompose rapidly when not buffered with water. Our approach entails the use of a membrane delivery system where 99.6% hydrogen peroxide is dissolved in an organic solvent (Figure 1a). Hydrogen peroxide gas permeates the membrane and is delivered to the process chamber, while the solvent does not permeate and remains in the liquid state.

Next generation devices have low thermal process constraints. Hydrazine ($H_2NNH_2$) is highly reactive and appears to be the ideal low temperature nitrogen passivation source. However, it is highly flammable, toxic and current commercial materials lack sufficient purity. In an analogous approach to hydrogen peroxide, we have developed a new method and formulation for the delivery

of anhydrous hydrazine by the use of an inert organic solvent and membrane delivery system (Figure 1b). Precursor vapor pressure is maintained at levels viable for current passivation process requirements. Moreover, the addition of a high boiling point solvent raises the solution flash point, reducing explosive risk.
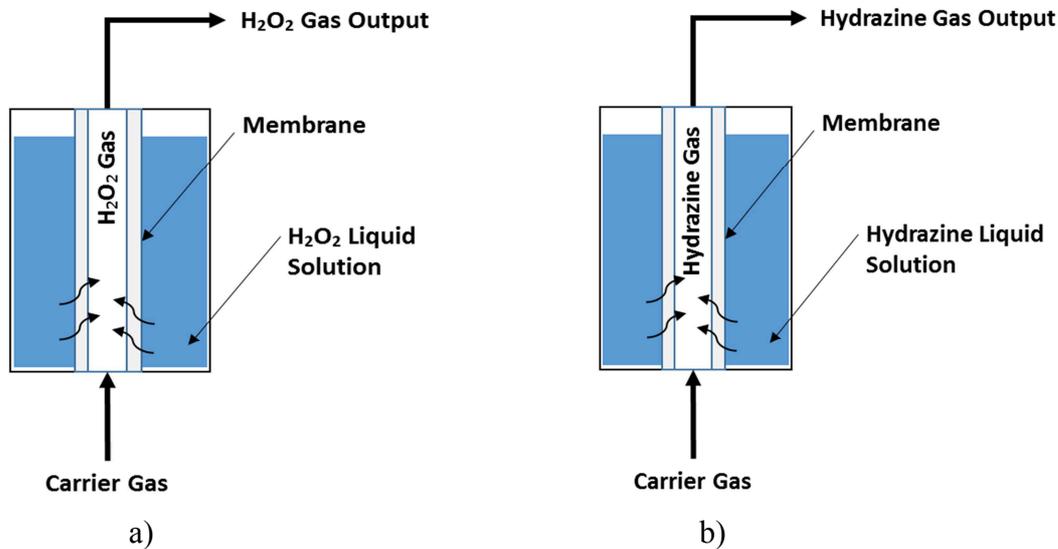


Figure 1. Novel Precursor Membrane Delivery System for a) anhydrous hydrogen peroxide ($H_2O_2$) and b) anhydrous hydrazine ($H_2NNH_2$).

**Passivation Methods**

Implementation of our novel sources focused on the passivation of InGaAs(001) and SiGe(110) surfaces.

A saturated Si-OH passivation layer was deposited on InGaAs(001)-(2x4) at a substrate temperature of 350°C. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of the saturated Si-OH layer on InGaAs(001)-(2x4). Oxidation by anhydrous hydrogen peroxide is self-limiting where underlying substrate damage is avoided. In contrast, oxidation with the use of HOOH/H2O gas mixtures shows oxidation of Indium with the resulting formation of Indium oxide.

The 350°C self-limiting surface passivation procedure included a decapped $In_{0.53}Ga_{0.47}As(001)$-(2x4) surface dosed with total 87.6 MegaLangmuir $Si_2Cl_6$ followed by 210.55 MegaLangmuir total anhydrous HOOH(g). Complete surface saturation of $Si-O_x$ on InGaAs(001)-(2x4) was determined to occur once no further increase in the O 1s peak was seen with additional anhydrous HOOH(g) doses (Figure 2).
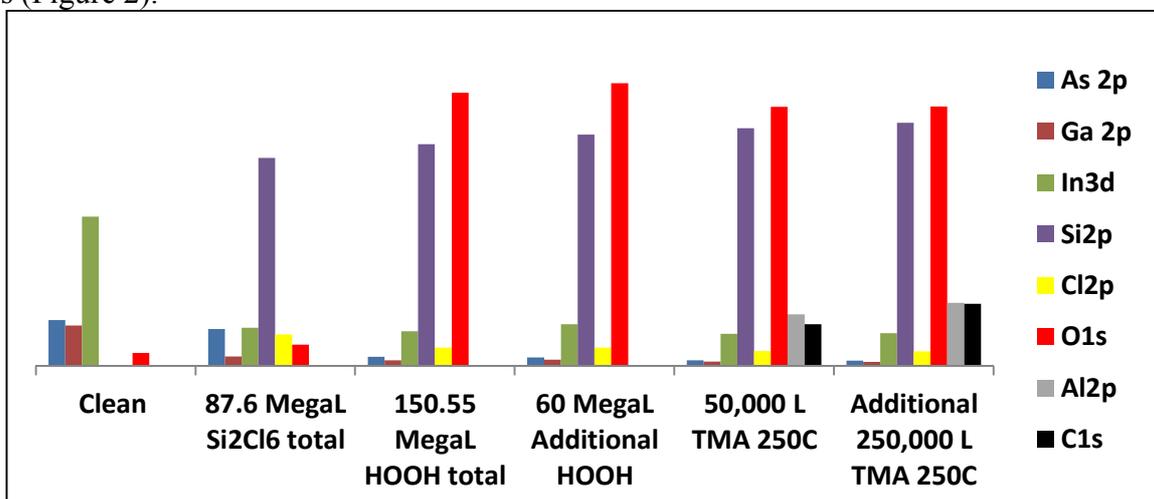


Figure 2. XPS characterization of the InGaAs(001) passivation study.

Following Si-OH surface saturation, 300,000 L TMA was dosed at 250°C, and XPS showed the emergence of Al 2p and C 1s peaks indicative of TMA surface nucleation. The surface was then dosed with 500 L atomic H at 250°C to replace the methyl groups on the surface aluminum with -H termination as well as remove any residual chlorine left on the surface. STS (Figure 3) shows that after hydrogen peroxide exposure, the surface Fermi level shifts toward the valence band due to the surface induced dipole from the presence of –OH and -O- groups. Subsequently, after capping with Aluminum, the surface Fermi level shifts back toward the conduction band.
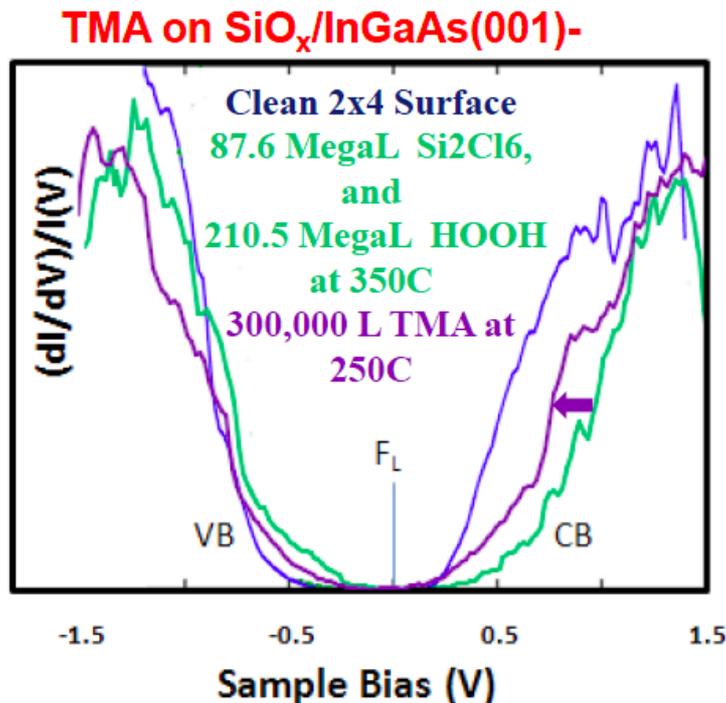


Figure 3. STS of a) Clean InGaAs(001) surface(blue), b) Shift toward the valence band due to the surface induced dipole after HOOH exposure, c) Shift back toward the conduction band after capping with TMA.

Figure 4 shows the XPS results from a similar experiment performed with aqueous 30% $H_2O_2/H_2O$ vapor. Here, the appearance of a large $InO_x$ peak is observed after exposure to hydrogen peroxide. In this case, it is evident that sub-surface oxidation has occurred and $InO_x$ has migrated to the surface. Therefore, while the use of anhydrous hydrogen peroxide leads to self-limiting surface oxidation, the presence of water is a detriment and damages the surface.
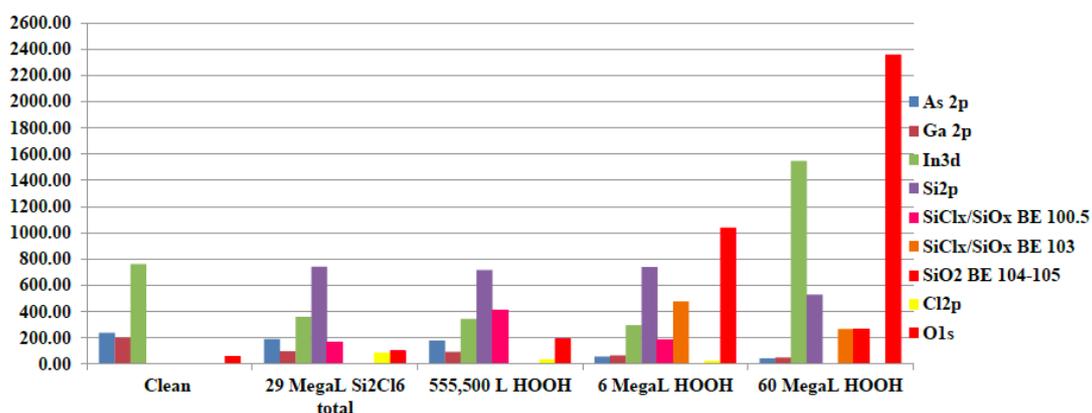


Figure 4. XPS of a $Cl_xSi$/InGaAs(001) surface treated with 30%H2O2/H2O. Indium migrates to the surface and forms $InO_x$.

The next part of our study focused on developing a low temperature silicon nitride passivation process for SiGe substrates. A silicon nitride passivation layer on semiconductor surfaces can serve several practical uses, such as acting as a diffusion barrier or channel passivation layer prior to dielectric deposition in FinFets or MOSFETs. When employed as a channel passivation layer, further reaction with an oxidant, such as anhydrous hydrogen peroxide, can leave Si-N-OH termination, which allows for further functionalization. STM/STS and XPS were employed to characterize $SiN_x$ film growth on $Si_{0.5}Ge_{0.5}(110)$.

The silicon nitride passivation procedure was carried out at a substrate temperature of 275°C and was performed on a p-type $Si_{0.5}Ge_{0.5}(110)$ surface (Figure 5). After a 315 MegaLangmuir anhydrous hydrazine dose, XPS showed $N-H_x$ surface termination, and removal of half of the initial carbon contamination. A subsequent 21 MegaLangmuir $Si_2Cl_6$ dose followed by 17 cycles of 3 MegaLangmuir hydrazine and 3 MegaLangmuir $Si_2Cl_6$ led to increased silicon nitride growth as shown by a large increase in XPS Si 2p and N 1s peaks, as well as a decrease in the Ge 3d substrate peak. STS of the atomic hydrogen cleaned surface (Figure 6) shows that the surface Fermi level is pinned at the midgap, the $SiN_x$ on SiGe(110) looks slightly more p-type with a bandgap size of 0.8-0.9 eV.



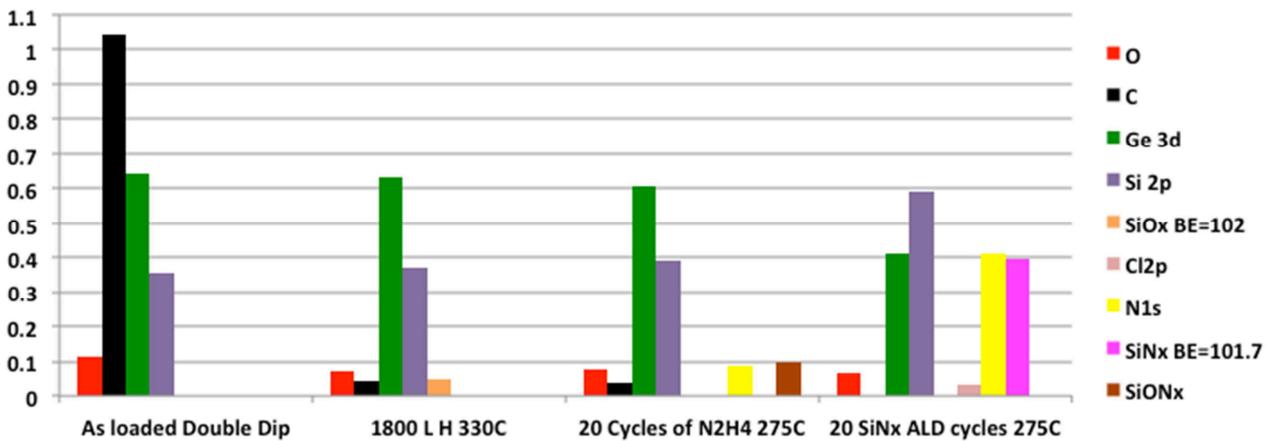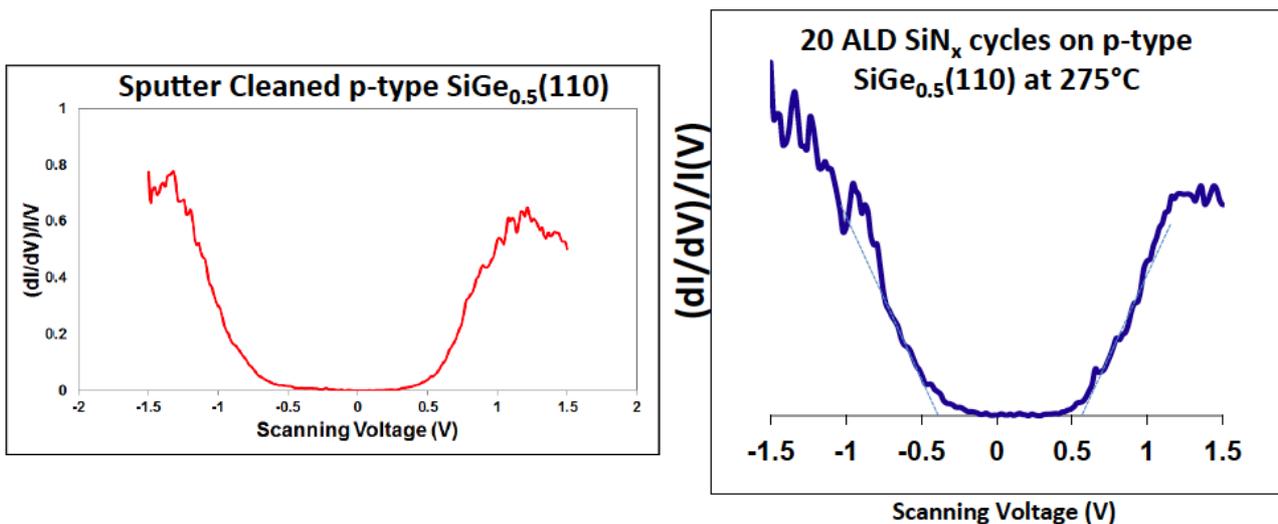Figure 5. XPS characterization of the SiGe(110) passivation study.



Figure 6. XPS of Cleaned Surface and $SiN_x$ surface.

**Conclusion**

In conclusion, the in situ dry cleaning and passivation requirements of future generation materials have made obvious the need for new gaseous passivation sources. We have demonstrated the ability to deliver anhydrous hydrogen peroxide and hydrazine with novel membrane delivery methods. Feasibility for in situ dry surface preparation and passivation has been demonstrated by the deposition of very thin layers of Si-OH and Si-NH without sub-surface damage.

**References**

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