THE INFLUENCE OF HYDROGEN ON THE DEFECTS AND INSTABILITIES
IN HYDROGENATED AMORPHOUS SILICON


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ABSTRACT

The presence of hydrogen in amorphous silicon alloys affects both the defect structure and the instabilities. Specific examples where the presence of hydrogen is either directly or indirectly important include (1) the elimination of silicon dangling bonds, (2) the trapping of molecular hydrogen in voids and (3) the presence of optically-induced, reversible metastabilities in the optical and electronic properties.

INTRODUCTION

In tetrahedrally coordinated amorphous alloys the therapeutic role of hydrogen in passivating "dangling bonds" is well known. In amorphous silicon without hydrogen (a-Si) the densities of silicon "dangling bonds" as measured by electron spin resonance (ESR) are almost always greater than $10^{18}$ spins cm$^{-3}$. With the addition of hydrogen the spin densities in a-Si:H can be as low as $10^{15}$ spins cm$^{-3}$.

Although the passivation of silicon dangling bonds is extremely important, especially for electronic applications, the presence of hydrogen has a much greater influence on the structure and the defects in a-Si:H than merely satisfying these dangling bonds. There may be $10^{21} - 10^{25}$ spins cm$^{-3}$ in a-Si, but typical samples of a-Si:H contain over $10^{17}$ hydrogen atoms cm$^{-3}$. Therefore, the vast majority of hydrogen atoms in a-Si:H serves to reduce the number of silicon-silicon bonds in the alloy. The common perception is that hydrogen atoms replace "strained" silicon-silicon bonds with silicon-hydrogen bonds. This process is thought to be especially prevalent on the surfaces of internal voids which remain even in the best device-quality alloys.

In addition to dramatically altering the local structural order and to passivating dangling bonds, the presence of hydrogen in amorphous silicon also affects the defect structure in more subtle ways. For example, several experiments have detected the presence of trapped molecular hydrogen ($H_2$ molecules) in a-Si:H. These molecules are probably trapped in small internal voids where they are stable up to fairly high temperatures ($> 500^\circ$C in many cases). Even though most a-Si:H alloys have considerable oxygen contamination ($\geq 10^{19}$ cm$^{-3}$), the
presence of OH groups in these alloys is very rare. The vast majority of the hydrogen is found to bond preferentially to silicon. In alloys with oxygen purposely added at levels of 1-2 at.\% one can trap atomic hydrogen, probably on oxygen-rich internal surfaces. An indirect influence of hydrogen on the defect structure in a-Si:H alloys involves the role of hydrogen in eliminating nonradiative processes such as those dominated by silicon dangling bonds. The presence of hydrogen allows efficient photoluminescence (PL) to occur, and the PL processes are strongly influenced by the hydrogen concentration in the alloys.

In addition to these examples of the influence of hydrogen on the formation of defects in a-Si:H, hydrogen may play at least an indirect role in the occurrence of electronic and optical metastabilities in the "best" a-Si:H alloys.* The first observation of such an effect was a decrease in the photoconductivity after optical excitation as reported by Staebler and Wronski. Since this work, metastable changes in many other transport and optical properties have been observed. Unfortunately, all of these changes, many of which may not be directly related, are often grouped together under one generic title as "the Staebler-Wronski effect." We shall discuss only one aspect of this effect, the occurrence of a metastable, optically-induced paramagnetism in a-Si:H.

DEFECTS

Although the dangling bond on the group IV atom is commonly considered to be the primary paramagnetic defect with an energy near the center of the gap, there are several other defects which are potentially important in determining the electronic properties of these alloys. In hydrogenated amorphous silicon the dangling bond defect yields an ESR response at $g \approx 2.0055$ which is always present on a level of at least $10^{15}$ spins cm$^{-3}$. In silicon-germanium alloys two ESR signals are generally observed, one attributed to a dangling bond on Si and the other to a dangling bond on Ge. The most common interpretation of these defects is that they are paramagnetic and neutral in the ground state, but it has also been suggested that at least some of the Si and Ge dangling-bond defects might exist positively and negatively charged (negative $U_{\text{eff}}$ system) in the ground state.

Several shallow defects near the band edges have been postulated in these alloy systems, but none of them directly involve the presence of hydrogen. The most accepted interpretation of these defects is in terms of strained bonds on the group IV atoms. It has also been suggested that neutral two-fold coordinated Si and Ge atoms may be responsible for these shallow electronic states.

The occupancy of many of these defects can be altered optically by the application of band-gap light. Three transient optically-induced ESR

*In the common perception, the "best" a-Si:H alloys are those whose electronic properties, such as photoconductivity, electronic mobility and so forth, yield the highest quality electronic devices. Since the technology is currently driven almost exclusively by photovoltaic or thin film transistor applications, the best usually translates into something like the highest solar cell efficiency or the fastest switching speed. In terms of the basic properties of the material, the best refers in some qualitative fashion to the lowest density of electronically-active defects. Perhaps the most accurate definition of the best a-Si:H alloys is those which exhibit the greatest instabilities in their electronic and optical properties.