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Hydrogen passivation of gold in p-type silicon involving hydrogen-gold-related deep levels

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We report on two hydrogen-gold-related deep levels ($G2$ and $G3$) in gold-doped p-type silicon. The levels are formed after hydrogenation by wet chemical etching. Using deep-level-transient-spectroscopy depth profiling and capacitance-voltage analysis we demonstrate that the levels are caused by injection of hydrogen into gold-doped silicon. The etching treatment results in a decrease of the gold-donor concentration, which can be fully explained by a corresponding increase of the $G2$ trap concentration. The results indicate that the $G2$ level belongs to an electrically active gold-hydrogen (Au-H) complex that changes into an electrically inactive Au-H complex upon heat treatment between 150 and 200 °C. Prolonged heat treatments within this temperature range result in dissociation of these electrically inactive Au-H complexes and the gold-donor concentration approaches its initial value.

Hydrogen is able to neutralize both shallow and deep centers in silicon.[1] It is normally introduced into silicon using remote hydrogen plasma,[2] but it is even possible to introduce hydrogen to a smaller extent by wet chemical etching.[3,4] Hydrogen passivation of the deep levels of gold was reported by Pearton and Tavendale[5] using remote plasma hydrogenation. The levels were passivated to depths less than 10 μm and were only partially regenerated by subsequent 2-h vacuum annealing at 400 °C. Following this discovery, hydrogen passivation of other transition-metal deep levels was systematically investigated.[6] Recently it has been observed that in some cases hydrogenation induces transition-metal-related deep levels. Hydrogen-related levels have been reported in silicon doped with gold,[7] vanadium,[8] chromium,[9] and silver.[10] The key to observing these levels is to keep the sample temperature close to room temperature during hydrogenation because these traps anneal out between 150 and 250 °C. This is most easily achieved by wet chemical etching.

In this paper we report studies on hydrogen passivation of gold in p-type silicon. We distinguish between two different gold-hydrogen complexes, one which is electrically active having deep levels within the silicon band gap and one electrically inactive observed indirectly as passivation of gold donors. We find that gold is not passivated by hydrogenation at room temperature. Instead, two new hydrogen-gold-related deep levels ($G2$ and $G3$) appear after the hydrogenation. The depth profiles of the gold donor and the new deep traps change drastically when atomic hydrogen in the surface region is driven deeper into the samples by applying a reverse bias during annealing. The sources of hydrogen are neutral boron-hydrogen pairs that dissociate during the heat treatment.

The samples were made from 2- or 3-in. ⟨100⟩-oriented Czochralski p-type boron-doped silicon wafers with thicknesses of 360–380 μm and resistivities in the range of 1–12 Ω cm. The wafers were coated with an approximately 1500-Å-thick gold layer on one side. The gold was then driven in at 893 °C for 4 h in nitrogen ambient. This resulted in a U-shaped gold-doping profile with gold-donor concentration between 2 and 4×10^{14} cm^{-3} in the middle region, depending on the substrate used. In order to obtain uniform gold concentrations approximately 50 μm was etched off the surfaces of the wafers using isotropic silicon etch (HNO_3:HF:CH_3COOH:$HClO_4$, 7.3:2.9:2:1). Schottky contacts were formed by evaporation of aluminum (Al) or by sputtering of titanium or aluminum at room temperature. GaAl alloy was rubbed into the reverse sides of the samples to obtain Ohmic contacts. Reference samples not doped with gold were made to certify that the effects observed were related to gold impurities. No deep levels were detected in these samples using deep-level transient spectroscopy (DLTS).

The experimental setup used in this study is a computerized DLTS system, the details of which have been described elsewhere.[11] The depth profiles of the deep traps were obtained with capacitance DLTS depth profiling taking into account the nonuniform doping profile due to hydrogen neutralization of boron acceptors. The heat treatments at temperatures ≤ 120 °C were performed in the dark within the cryostat in helium ambient. The hole capture cross sections were measured by majority carrier pulse filling.[12]

First we demonstrate that hydrogen is injected into the surface region during etching. The active boron acceptor concentration after etching was estimated using C-V profiling. Figure 1(a) shows a typical evolution of the net active acceptor profile in a reference sample at 80 °C using a reverse bias of 8 V. The steep increase of some of the profiles at depths below 0.5 μm is an artifact of the measurement. The reactivation of the boron acceptors in the region 0.5–0.6 μm followed simple first-order kinetics for all annealing times in the temperature range 40–120 °C, provided that a reverse bias was applied to the sample during annealing (RBA).

In Fig. 1(b) we compare the reactivation rates with data from the literature on dissociation of boron-hydrogen (B-H) complexes. The dissociation rates are estimated from a series of RBA at different temperatures using the approach of Zundel and Weber.[13] We obtain an activation energy of dissociation of 1.28 eV and an attempt frequency of 2.2×10^{14} s^{-1} in excellent agreement with the detailed studies of Zundel and Weber[13] who obtained 1.28 eV and 2.8×10^{14} s^{-1}.

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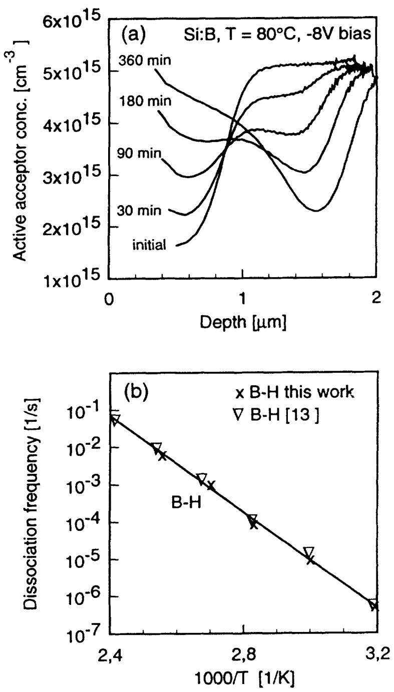

FIG. 1. Reactivation of boron dopants after wet chemical etching estimated from C-V profiling. (a) Boron reactivation and neutralization at 80 °C at a reverse bias of 8 V. (b) Reactivation rates of boron compared to literature data (Ref. 13) on dissociation of B-H pairs.

A typical DLTS spectrum of a gold-diffused sample after etching is shown in Fig. 2, curve 1. No less than five DLTS peaks are observed and the most prominent one is the gold-donor peak with an activation energy $\Delta E = 0.36$ eV (using T^2 adjustment) and a hole capture cross section $\sigma_p = 1.5 \times 10^{-15}$ cm^2 measured at 162 K. Spectrum 2 was taken after heat treatment at 120 °C for 30 min. The peaks labeled $G2$ and $G3$ (Ref. 14) increased after the heat treatment while the gold-donor peak decreased. The $G2$ level has an activation energy of 0.21 eV and a hole capture cross section of 1.7×10^{-15} cm^2. No temperature dependence of this cross section was found in the temperature range 100–125 K. The $G3$ peak has an activation energy of 0.47 eV and a hole capture cross section of 5×10^{-16} cm^2 measured within the temperature range 228–250 K. The peak at approximately 280 K is probably due to a small change in the population of the gold-acceptor level.[15] Finally, the weak signal at 180 K has not been identified. It anneals out during heat treatment of 30 min at 150 °C.

Figure 3 shows the effect of reverse bias annealing on the depth profiles of the net acceptor concentration and the gold-donor $G2$ and $G3$ concentrations. Two samples were annealed at 120 °C for 10 min at 0 (a) and -5 V bias (b). There is a clear correlation between the active boron-acceptor profiles and the profiles of the deep traps. Prior to annealing boron acceptors are passivated in the surface region. The $G2$ and $G3$ traps are only found within the hydrogenated region and a corresponding decrease in the gold-donor concentration is also observed. Annealing without bias results in minor changes of all profiles closest to the surface: the gold-donor concentration decreases while the $G2$ and $G3$ concentrations increase. The effect of reverse bias is more dramatic. The B-H pairs closest to the surface dissociate and the released hydrogen neutralizes boron acceptors near the depletion layer edge at about 1.6 μm. Simultaneously, the gold-donor concentration decreases close to the depletion layer edge while the $G2$ concentration increases by roughly the same amount. A similar effect of the reverse bias is seen on the $G3$ depth profile. We repeated this experiment using different values of the reverse bias and found that the changes in the depth profiles always followed the depletion layer edge. No significant changes of the trap profiles were observed if the samples were annealed under a reverse bias at lower temperatures where the B-H pairs are stable.

The results above demonstrate that $G2$ and $G3$ are re-

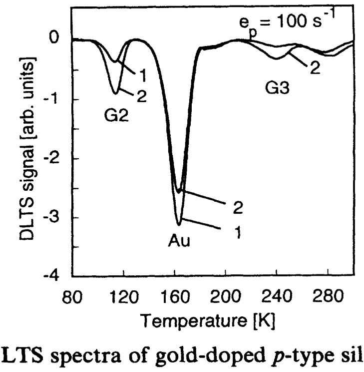

FIG. 2. DLTS spectra of gold-doped p-type silicon. Curve 1, after etching, curve 2, after heat treatment at 120 °C for 10 min. Reverse bias 5 V, filling pulse 5 V.

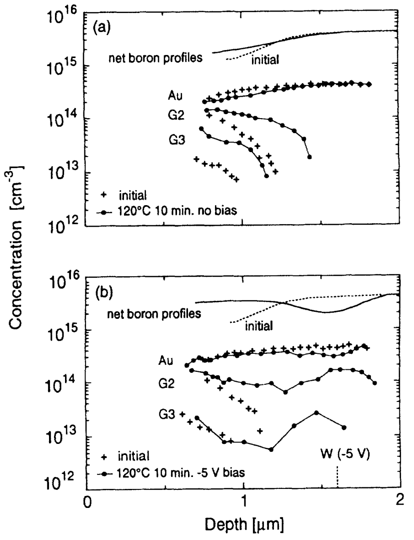

FIG. 3. The effect of reverse bias annealing on the depth profiles of the net boron-acceptor concentration and the gold donor, $G2$ and $G3$ concentrations estimated from capacitance-voltage analysis, and DLTS depth profiling. (a) Depth profiles before and after heat treatment at 120 °C for 10 min. (b) Depth profiles after the same heat treatment as in (a) with a reverse bias of 5 V during the annealing. The depletion layer depth W during the reverse bias annealing is also indicated.

lated to atomic hydrogen and the gold donor. It should be pointed out that the increase of the $G2$ concentration fully accounts for the decrease of the gold-donor concentration after hydrogenation. This was true for annealing of 30 min below 150 °C with or without applied bias. Annealing at 150 or 175 °C for 30 min resulted in passivation of gold donors, partial dissociation of $G2$, and complete dissociation of B-H pairs.

Figure 4 shows the concentrations of the deep traps in two samples annealed repeatedly without bias at 150 and 175 °C, respectively. The concentrations were estimated using DLTS depth profiling in a region (0.9–1.2 μm) where the trap concentrations were approximately uniform. In Fig. 4(a) we note that the concentrations of all the deep traps decrease during the first annealing step, both at 150 and 175 °C in contrast to the results shown in Figs. 2 and 3. The decrease of the gold-donor concentration during the first annealing steps is possibly related to a complete dissociation of the B-H pairs. If so, some of the released hydrogen passivates the gold donors instead of forming $G2$ and $G3$ traps which are not thermally stable at these temperatures. Another important result in Fig. 4(a) is that the annealing of $G2$ is not accompanied by an increase of the electrically active gold-donor concentration. This indicates that the gold involved in $G2$ becomes electrically inactive (i.e., passivated) when the $G2$ traps anneal out.

Figure 4(b) shows how gold donors are reactivated during prolonged heat treatments at 175 °C. The gold concentration decreases during the first annealing step but recovers slowly with annealing time and about 80% of the passivated gold atoms are reactivated after 19 h. $G2$ appears to anneal out in a two-stage process and the slow dissociation at long annealing times (> 2 h) seems to follow the reactivation of gold donors. Using the data in Fig. 4(b) we can estimate the dissociation rate of $G2$, and the reactivation rate of passivated gold donors, at long annealing times (≥ 2 h). It turns out that both these rates are approximately 2×10^{-5} s^{-1}. More data at different temperatures is needed to check this trend. Still, this result indicates that there is a certain equilibrium between the concentrations of $G2$ traps and electrically inactive Au-H complexes (i.e., passivated gold).

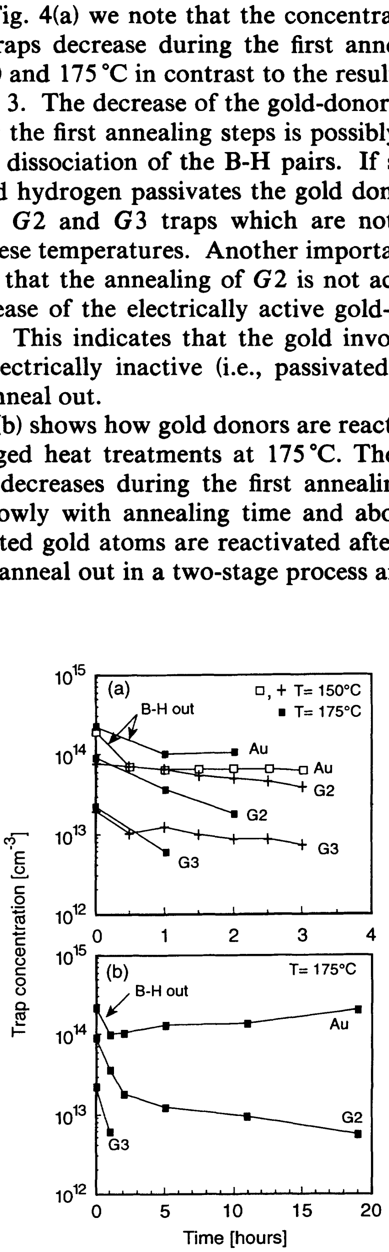

FIG. 4. Concentrations of gold donors $G2$ and $G3$ as functions of annealing times at 150 and 175 °C. Two samples were annealed repeatedly at 150 and 175 °C, respectively. The $G3$ concentration after 2 h at 175 °C is below the detection limit ($< 3 \times 10^{12}$ cm^{-3}).

There is a strong correlation between $G2$ and $G3$ regarding depth profiles and annealing behavior. However, the estimated trap concentration of $G3$ is always much lower than the $G2$ trap concentration suggesting that the two levels do not belong to the same recombination center. The levels $G2$ and $G3$ anneal out in the same temperature range as the hydrogen-gold-related acceptor level previously reported in n-type Si, labeled $G1$.[7] Still, $G1$, $G2$, and $G3$ have not yet been observed in the same sample so it is not clear if they all appear simultaneously after hydrogenation.

One clear difference is observed between hydrogenation of gold doped n- and p-type silicon by etching at room temperature. In p-type samples we can explain the decrease of the gold-donor concentration after etching by formation of the new trap $G2$. This is not the case in n-type samples where part of the gold acceptors closest to the surface are neutralized.[7] The neutralization in n-type material is possibly due to Coulombic attraction between the ions involved. It is well established that interstitial atomic hydrogen is positively charged in p-type material while most theoretical and experimental studies indicate that hydrogen is mainly neutral or negatively charged in n-type silicon.[16–18] Sadoh, Nakashima, and Tsurushima[8] found that hydrogen induced by chemical etching enters n-type silicon predominantly as a positively charged species. In addition, Johnson and Herring[19] recently demonstrated that most of the atomic hydrogen within the space charge region in n-type silicon is positively charged. It is therefore possible that gold acceptors are passivated by H^+ close to the surface in n-type samples at room temperature. However, the observed neutralization of gold in p-type silicon at 175 °C cannot be explained by such a Coulombic attraction since the occupancy of the gold-acceptor level is negligible at that temperature.

From the annealing data shown in Fig. 4 we note that the reactivation of passivated gold donors appears to be much faster than previously observed.[5,6] This was also the case for reactivation of passivated gold acceptors in n-type silicon after wet chemical etching.[20] In this study gold is almost fully reactivated after 19 h at 175 °C while heat treatment of 2 h in vacuum at 400 °C resulted in partial regeneration of gold in the original studies of Pearton and Tavendale.[5] Still, the actual kinetics of the reactivation have not yet been thoroughly measured and it is therefore not clear if the passivation mechanism is the same in these two studies.

Since the levels $G2$ and $G3$ anneal out above 150 °C they have not been observed in previous passivation studies using remote plasma hydrogenation at temperatures above 150 °C.[5,6] However, levels in gold-doped silicon with similar annealing behavior and depth distributions have been reported by Lemke.[21]

In summary we observe two hydrogen-gold-related deep levels in *p*-type gold-doped silicon after hydrogenation by wet chemical etching. The levels anneal out within a few hours at temperatures between 150 and 200 °C and the gold atoms involved become electrically inactive (i.e., passivated). No gold passivation occurs in *p*-type material below 150 °C in contrast to previous studies on *n*-type samples where gold was passivated at room temperature.[7] Finally, passivated gold donors are readily reactivated within a few hours at temperatures between 200 and 250 °C.

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