

Hydrogen passivation of gold-related deep levels in silicon

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The passivation by reaction with atomic hydrogen of the well-known deep donor and acceptor levels associated with gold in silicon has been observed with the use of deep-level transient spectroscopy. The concentration profiles of the two centers are presented as a function of the duration and temperature of the exposure to atomic hydrogen: When exposed for 2 h at 350°C, less than 5×10^{-3} of the originally electrically active deep donors and acceptors remained to a depth of approximately 7 μm . Slight but significant differences in the concentration profiles of the electrically active defect centers after reaction with the atomic hydrogen may be additional evidence that the gold donor level and gold acceptor level are not related to the same center.

Extensive examination of gold in silicon has resulted in accurate measurements of its solubility and coefficient of diffusion over a wide temperature range and a good understanding of its electrical properties.¹ The practical importance of gold as a deep-level impurity in silicon is seen in its wide use as a lifetime control impurity.²⁻⁴ Recently it has been shown that the gold donor level and gold acceptor level are not related to the same center, as previously believed, and indeed that many other impurities in silicon create deep levels with similar electron thermal emission rates to that of the gold acceptor.⁵ The evidence presented by Lang *et al.* indicated that the gold acceptor was of complex structure, possibly involving lattice vacancies.⁵ The purpose of this Communication is to show that both the gold-related deep donor and acceptor levels in silicon may be passivated by reaction with atomic hydrogen, and to present data on the depth to which passivation of the defects as a function of the time and temperature of the hydrogen exposure can be affected. There is increasing interest in the use of atomic hydrogen as a passivant for defective bands associated with deep-level impurities in semiconductors, and the technique appears to have quite general application to both point⁶⁻⁹ and line¹⁰⁻¹² defects.

Both *n*- and *p*-type silicon were used in this study. The *n*-type material was phosphorous doped with a resistivity of $\sim 7 \Omega \text{cm}$ (Czochralski) and the *p*-type material was boron doped with a resistivity of $\sim 20 \Omega \text{cm}$ (float zoned). Gold was evaporated onto one face of the wafers, and then diffused for 10 h at 1175°C to produce uniform doping. A phosphorus diffusion for 0.5 h at 975°C formed an abrupt *n*⁺*p* step junction for the *p*-type samples, and provided an Ohmic contact for the *n*-type samples. Finally, gold was evaporated onto the other face of the samples to provide an Ohmic contact for the *p*-type diodes, and a rectifying contact for the *n*-type samples. The *p*-type

samples were approximately 700 μm thick and the *n*-type samples approximately 75 μm thick. The net acceptor concentration in the completed *n*⁺*p* junctions was found to be $8 \times 10^{14} \text{cm}^{-3}$, while the net donor concentration in the Schottky diode *n*-type samples was $6 \times 10^{14} \text{cm}^{-3}$.

Deep-level transient spectroscopy (DLTS)¹² measurements on the samples revealed the two dominant gold-related defects. Figure 1(a) shows the typical DLTS spectrum obtained from the *n*-type samples, together with a complementary measurement, a thermally stimulated capacitance (TSCAP)^{13,14} scan. The DLTS peak represents the gold acceptor level, which gave a measured activation energy of 0.55 eV (with T^2 correction) from the conduction band. The capture cross section for electrons for this level was measured as $1.8 \times 10^{-16} \text{cm}^2$ at 265 K, using the bias-pulse method described by Henry *et al.*¹⁵ These parameters are in good agreement with Lang *et al.*,⁵ who used *n*-type material with similar characteristics. The concentration of the acceptor level was $2.3 \times 10^{13} \text{cm}^{-3}$, constant throughout the depletion region investigated (7.2 μm).

In the *p*-type material, a single DLTS peak representing the gold-related donor level was observed, as shown in Fig. 2(a). The activation energy of this level was measured to be 0.34 eV from the valence band, with a capture cross section for holes of $1.9 \times 10^{-15} \text{cm}^2$ at 160 K, in good agreement with previous measurements,^{16,17} taking into account the apparent temperature insensitivity of the cross section.⁵ The concentration of the donor level was $9 \times 10^{12} \text{cm}^{-3}$, constant over the region investigated (7.1 μm).

Samples were exposed to atomic hydrogen by insertion in a 0.5-W cm^{-3} (limiting upper value) radio-frequency-induced (27 MHz) hydrogen plasma, at a pressure of approximately 0.5 Torr. The plasma was created by rf power inductively coupled by a coil en-

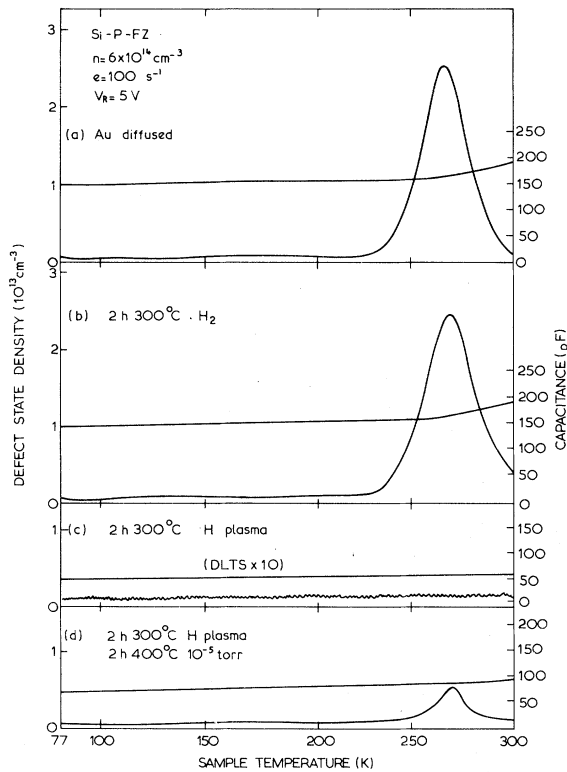


FIG. 1. DLTS spectra and TSCAP scans recorded under the same conditions of trap emission rate ($E = 100 \text{ s}^{-1}$) and reverse bias ($V_R = 5 \text{ V}$) corresponding to a depletion depth of $3.1 \mu\text{m}$. (a) Au-diffused n -type Si, showing the gold-related acceptor defect peak. (b) Following a 2-h, 300°C anneal in H_2 , showing no change in defect concentration. (c) Following a 2-h, 300°C anneal in a H plasma, showing significant reduction in the electrically active defect concentration. (d) Following a 2-h, 300°C plasma exposure and subsequent 2-h 400°C vacuum anneal at a pressure of approximately 10^{-5} Torr. Reappearance of the acceptor centers is evident.

veloping a quartz tube; samples were mounted on a high-purity silicon substrate placed on a heater pedestal. After exposure to the plasma for a period of 2 h at temperatures of $150\text{--}350^\circ\text{C}$, the samples were allowed to cool in the plasma until their temperatures had reached 80°C (maximum time required approximately 45 min). Molecular hydrogen anneals were performed similarly, without the plasma. All samples subjected to atomic- or molecular-hydrogen heat treatments had their gold barrier or Ohmic contacts evaporated on after the heating.

Figures 1(b) and 2(b) show the DLTS spectra for n - and p -type samples heated in molecular hydrogen for 2 h at 300°C ; heat treatment in H_2 for any of the times and temperatures used here had no effect on the concentration or constancy of the profile for either the donor or acceptor levels.

Heating the samples in the hydrogen plasma, how-

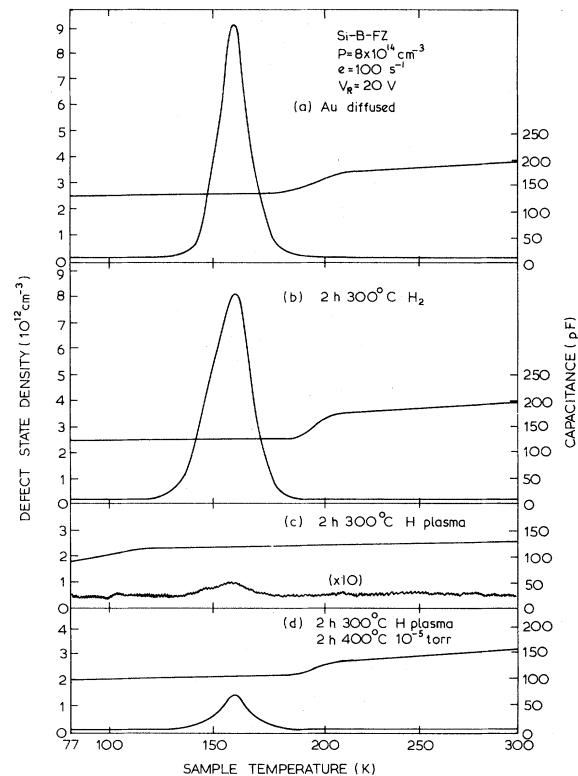


FIG. 2. Analogous results from the gold-related donor center in p -type Si to those displayed in Fig. 1 for the gold-related acceptor center in n -type Si. The only difference in spectra conditions is that, here, a reverse bias of 20 V was used, corresponding to a depletion depth of $5.8 \mu\text{m}$.

ever, significantly reduced the density of the electrically active gold-related defect centers. Figures 1(c) and 2(c) show the DLTS spectra recorded for n - and p -type samples heated for 2 h at 300°C in the H plasma. Supportive evidence for the observed neutralization of the deep-level centers comes from the TSCAP scans, which show a reduction in sample capacitance for both material types.

Annealing the samples *in vacuo* (10^{-5} Torr) for 2 h at 400°C after a prior hydrogenation produced a reappearance of some of the electrically active defect states, as shown in Figs. 1(d) and 2(d). This is probably due to two effects: emission of the atomic hydrogen from the samples, and recombination of the H to H_2 in the bulk of the material. Control samples initially without gold contamination showed no gold-related levels after a similar vacuum anneal.

Plasma exposures at various temperatures were carried out. Figures 3 and 4 show the concentration profiles of the gold acceptor and donor levels, respectively, obtained from DLTS measurements, as a function of the plasma exposure conditions. The concentrations after plasma treatment are normalized to the original pretreatment values to allow compar-

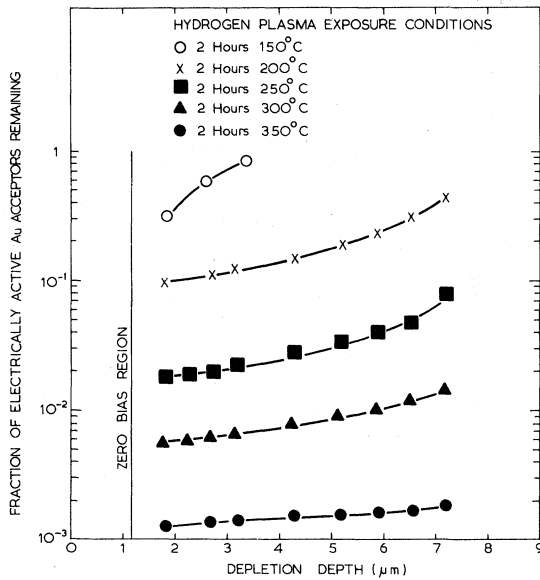


FIG. 3. Concentration profile of the gold-related acceptor defect ($E_c - 0.55$ eV) in n -type Si as a function of the duration and temperature of the exposure to atomic hydrogen. The zero-bias depletion depth is approximately $1.2 \mu\text{m}$ for the material used here.

ison of the efficiency of the atomic hydrogen in neutralizing the acceptor and donor centers. The zero-bias depletion depth for both types of material was approximately $1.2 \mu\text{m}$, assuming a built-in bias of approximately 0.85 V ,¹⁸ and thus measurements cannot be made in this region. After a 2-h exposure at 350°C , less than 5×10^{-3} of the original electrically active defect centers remained to a depth of about $7 \mu\text{m}$. Lower-temperature exposures for the same time were less efficient but still led to significant centralization of both the acceptor and donor centers. The forms of the concentration profiles are related to the temperature dependence of the solubility and diffusion coefficient of hydrogen in silicon, and to the nature of the passivation mechanism of the hydrogen with the ionized acceptor and donor levels. It is worth noting that for similar plasma exposure conditions, the gold-related acceptor is more efficiently passivated than the gold-related donor, typically by a factor of about 2. This may be due to subtle ion-pairing effects between the shallow donors in the n -type material and the gold-related acceptors,⁵ or more simply due to the fact that the gold-related acceptor and gold-related donor are not related to the same center,⁵ and may have different susceptibilities to neutralization by reaction with atomic hydrogen.

Using etch-decoration methods as well as direct determination by nuclear analysis,¹⁹ hydrogen was detected in the subsurface regions only in those silicon samples exposed to the plasma, supporting our

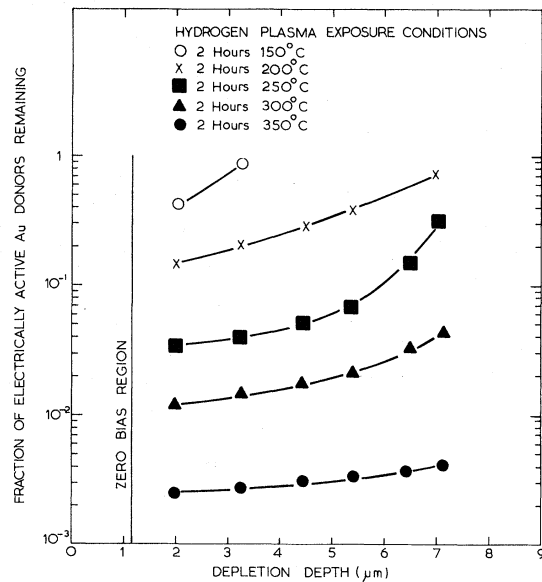


FIG. 4. Concentration profile of the gold-related donor defect ($E_v + 0.34$ eV) in p -type Si as a function of the duration and temperature of the exposure to atomic hydrogen. Note that on comparison with Fig. 3, the donor level is less susceptible to neutralization by reaction with the atomic hydrogen than is the acceptor level.

interpretation that the passivation of the deep-level gold centers is indeed due to reaction with atomic hydrogen. We consider it unlikely that the observed effect could in some way be due to absorption of light emitted from the plasma glow discharge, since the enhancement of the passivation effect at greater depths with increasing temperature, as seen in Figs. 3 and 4, would be unexpected. This latter effect is more simply explained by the increased diffusion rate of atomic hydrogen at higher temperatures.

In conclusion, we have reported the first direct observation of hydrogen passivation of gold-related deep acceptor and donor levels in silicon, together with some data on the depth of passivation as a function of the duration and temperature of the exposure to atomic hydrogen. The low temperatures ($\leq 350^\circ\text{C}$) and practical times (several hours) required to neutralize gold-related centers to depths of $\leq 10 \mu\text{m}$ gives hope that the technique may be useful in passivating defects induced during device processing.⁶ The study of the interaction of hydrogen atoms with crystal imperfections will hopefully lead to new insights into the nature of these defects.

ACKNOWLEDGMENT

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