Deep-level transient spectroscopy study on direct silicon bonded (1 1 0)/(1 0 0) interfacial grain boundary

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Abstract
In this paper, the electrical properties of direct silicon bonded (1 1 0)/(1 0 0) silicon interfacial grain boundary (GB) have been investigated by deep-level transient spectroscopy (DLTS) technique. The behavior of charge emission at the GB indicates that the GB states are localized. Since the hole capture unavoidably comes into the rate window to play an important role in the process of GB charge decay when the GB–DLTS signal reaches the maximum, the routine Arrhenius plot is not suitable to achieve the signature of the GB states. Then a double-pulse approach by subtracting the spectra, taken under different pulse voltages, has been applied to reveal the GB states in the energy range $E_v + 0.34$–0.42 eV with the hole capture cross-sections of 10^{-17}–10^{-16} cm^2. The obtained energy levels are close to the quasi-Fermi levels determined at the corresponding pulse voltages by current–voltage (I–V) measurements. These GB states are believed to be the intrinsic distorted bonds related to the GB.

(Some figures in this article are in colour only in the electronic version)

A number of studies have been devoted, in the past, to the nature and properties of grain-boundary (GB) states in polycrystalline silicon [1–4]. The barrier height is readily determined from capacitance– and current–voltage (C–V, I–V) characteristics [5], and the GB state density can then be derived by an appropriate deconvolution [6]. Meanwhile, both the density of states and the capture cross sections can be obtained more directly from the transient response after voltage pulses [7, 8]. However, the deep-level transient spectroscopy (DLTS) technique, as a powerful method for determining the signature of defect states, has seldom been applied to investigate the electronic states at the GB. A clear understanding of the GB–DLTS signal is needed, which is one objective of this paper. Meanwhile, for investigating the electrical properties of GB, an obvious difficulty is to separate the intrinsic GB effects from the extrinsic ones due to the presence of impurities, such as oxygen segregation [9]. The nature of the intrinsic GB states, e.g. band-like or localized, is still controversial [3, 7]. Recent advances in direct silicon bond (DSB) wafer with a shallow interface offer us a new opportunity to perform this investigation on an 'ideal' GB because the interfacial oxygen can easily be out-diffused by an elevated temperature annealing [10]. In this paper, we have reported a DLTS study on the clean shallow GB created by direct silicon bonding of a (1 1 0)/(1 0 0) wafer. It is found that the nature of the intrinsic GB states is localized and a double-pulse DLTS method can well define the signature of the GB state. These results should be of interest for both advanced integrated circuit and photovoltaic silicon.

The starting wafers were p-type (1 1 0) wafer with hydrogen implantation and (1 0 0) wafer, and then were directly bonded to create a large-angle (1 1 0)/(1 0 0) GB. The boron concentrations of both wafers are 9.28×10^{14} cm^{-3}. The upper (1 1 0) wafer was thinned to 200 nm thickness by layer-transfer technology plus chemically mechanical polishing [10], so that the oxygen impurities can easily be removed from this shallow interface to create a clean GB by a controlled high-temperature annealing. The interfacial oxygen concentration was clarified below the detection limit of secondary ion mass spectroscopy (SIMS) technique. For
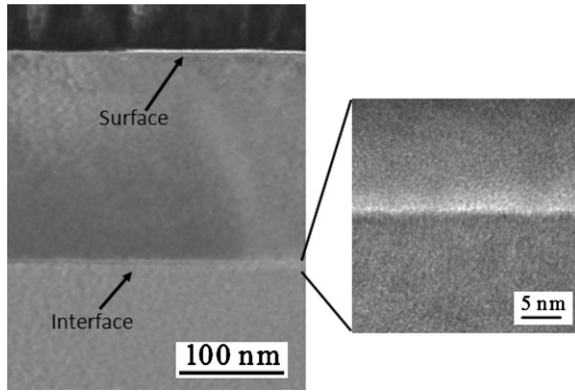
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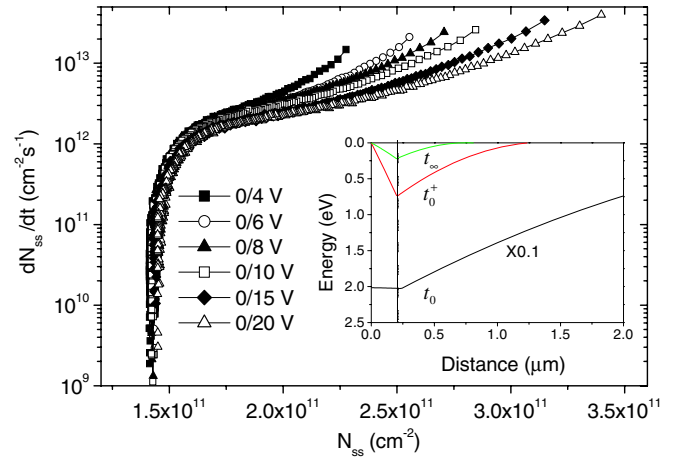**Figure 1.** TEM micrographs of the cross section of DSB wafer.

Figure 2. The GB charge decay rate as a function of charge density at zero bias after applying different positive pulse biases with a period of 200 ms on the Au contact at 260 K. The inset is the calculated energy band diagram near the GB at different times after filling the states by applying 20 V pulse voltage on the Au contact.

the electrical characterization, Ohmic contacts were formed on the upper (1 1 0) layer by preparing a 1 mm diameter Au contact and on the backside by scratching the InGa eutectic solution. Then, a Bio-Rad DL8000 Fourier transform digital deep-level transient spectroscopy system (1 MHz) was used to perform *I–V*, capacitance transient and DLTS measurements on the GB. The filling pulse biases were positively applied on the Au contact to inject the holes into the GB.

Figure 1 shows the TEM micrograph for the cross-section of our DSB wafer. Note that the bonding interface is exactly located at a depth of 200 nm beneath the silicon surface and meanwhile, no visible defects such as oxygen precipitates can be found at the GB in the high resolution TEM image. It is well known that the amount of charges at a silicon GB can be determined capacitatively. Since the present GB is located at a shallow depth of 200 nm beneath the sample surface, the GB built-in barrier can always deplete the thin upper layer [10]. Using the Poisson equation [11] and meanwhile, neglecting the difference of the work function between gold and the present silicon sample, the GB charge density (N_{ss}) under a bias *V* can be derived from the measured structural capacitance (*C*) as follows:

$$\frac{qN_A d_R^2}{2\varepsilon} - \frac{qN_{ss}d_1^2}{\varepsilon} = V, \qquad d_R = \frac{A\varepsilon}{C}, \qquad (1)$$

where N_A is the dopant concentration, ε is the dielectric constant of silicon, $d_1 = 200$ nm is the upper layer thickness, d_R is the total depletion width and *A* is the area of gold contact. Based on equation (1), the capacitance transient can be converted into the GB charge transient and then the charge decay rate on the GB states as a function of charge density can be derived by differentiating the charge transient for time, similar to the method used by Seager [7].

Figure 2 plots the charge decay rate as a function of the interface charge density at zero bias after applying different positive pulse biases on the Au contact at 260 K and the inset is the calculated energy band diagram near the GB at different times during and after applying a 20 V pulse bias on the Au contact. Under the filling pulse bias, some GB states with energies below the Fermi level at zero bias go above the Fermi level and capture holes to reach a new steady-state equilibrium [9]. The hole occupancy of these states obeys a quasi-Fermi distribution at the end of pulse, e.g. at t_0^-. When releasing

the filling pulse bias to zero, e.g. at t_0^+, a GB potential barrier larger than the equilibrium value immediately forms for both sides of the GB due to the initially filled charges. As the non-equilibrium charges emit, the GB barrier becomes smaller and smaller until it reaches the equilibrium barrier at t_∞ when all the non-equilibrium charges have emitted from the GB. It should be noted that when the GB potential barrier is not larger than the equilibrium value by several kT, the hole capture of GB states starts to become important [3, 7] and drastically decreases the charge decay rate. Therefore, a final fast drop of charge decay rates near the equilibrium GB charge densities has been seen in figure 2. Before this, e.g. at a large GB barrier, the GB charge decay can be considered to be due to a pure process of hole emission.

More interestingly, the GB charge decay rates due to hole emission in the curves of $dN_{ss}/dt \sim N_{ss}$ obtained by different pulse biases are not equivalent at the same charge densities. This result actually gives important information about the nature of GB states. Usually, the states associated with extended defects are classified as either band-like or localized if the rate of internal transitions is smaller or larger than the rate of carrier exchange with the valence or conduction band [13]. For band-like GB states, the rate of hole transition among them is much larger than that between the states and valence band [13]. Therefore, the total hole occupation of the GB states always keeps a time-dependent quasi-Fermi distribution and the holes only emit from the GB states with energy positions close to the variable quasi-Fermi level [7, 13]. As a consequence, the GB charge decay rate should remain constant at a certain charge density. For localized GB states, the rate of hole transition among them is much slower than that between states and valance band [13], and therefore each state almost exchanges the holes with valence band separately [3]. During the hole-emission process, the hole occupancy of various states always changes with time independently. Since the hole emission rate of states sharply depends on their energy positions (exponential law), the holes at shallower levels emit
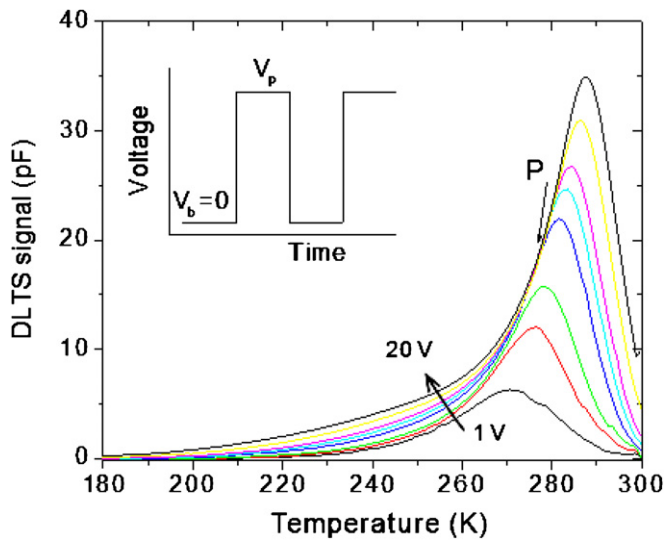
Figure 3. The GB–DLTS spectra obtained by applying different positive pulse voltages with a period of 200 ms on the Au contact (P is the inflection point).

Figure 4. The spectra obtained by subtracting the spectra obtained by applying different positive pulse voltages in figure 2.

much faster than those at deep levels and therefore give a main contribution to the hole emission in the initial part of transients [3]. Later on, the deep levels will dominate the process of hole emission. Thus, comparing the charge decay rates due to hole emission at the same charge density in the curves of $dN_{ss}/dt \sim N_{ss}$ obtained by different filling pulse widths, a smaller GB charge decay rate should be seen in the case of initially large charge density because more holes have already been emitted from the shallower levels and the hole emission mostly takes place from the relatively deeper levels. Thus, we can judge that the electronic states at the present GB are localized.

When the hole emission dominates the relaxation of the GB states, the hole emission rate (e_p) at an energy level (E_T) can be given by [11]

$$e_p = \sigma_p \gamma T^2 \exp\left(-\frac{E_T}{kT}\right), \qquad (2)$$

where σ_p is the hole capture cross-section, γ is a constant, T is the absolute temperature and k is the Boltzmann constant. With the Fourier transformed DLTS technique [14], the GB–DLTS signal represented by Fourier coefficients is determined by a rate window setting (the delay time t_0 and period t_W), as with the boxcar method. Figure 3 plots the GB–DLTS spectra obtained by applying different positive pulses on the Au contact. Note that all the spectra exhibit a single peak with a broad tail on the low-temperature side, while the peak maximum shifts to higher temperature with increasing pulse voltage. According to equation (2), it is known that the hole emission rate at each localized state exponentially depends on the energy position and temperature. Therefore, the initial rise of the GB–DLTS signal at low temperatures can be attributed to the hole emission from the shallower localized states. As the temperature increases, the deep levels come into play in the rate window until the signal goes to zero. The hole-capture process mentioned above in figure 2 starts to affect the GB–DLTS signal at the temperature at which an inflection point
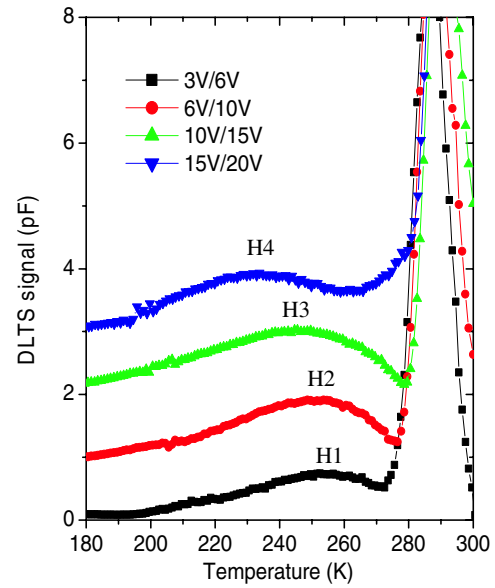
(see P in figure 3) occurs on the low-temperature side of the peaks. A peak maximum is reached when the charge decay rate from all the states equals $\ln[(t_0 + t_W)/t_0]/t_W$. Then the GB–DLTS signal goes to zero where the hole emission rate for all states becomes larger than t_0^{-1} at high temperature. Thus, it is understandable that an initially larger charge density obtained under a higher filling pulse voltage, essentially delays the hole-capture process. As a result, the inflection point and the peak maximum temperature in the GB–DLTS spectra shift to higher temperature with increasing filling pulse voltage. Since the maximum GB–DLTS signal contains the contribution of hole captures, the Arrhenius plot obtained at this point cannot correctly define the signature of GB states. Nevertheless, one can note that the GB–DLTS signal at the low-temperature side of the spectrum increases and becomes broader with pulse voltage increasing, which suggests a set of unresolved signal peaks related to localized shallower states.

In order to deconvolute these unresolved signals, we have subtracted the spectra obtained with different pulse voltages, as shown in figure 4, in which the principle is similar to the double-pulse DLTS (DDLTS) technique [15, 16]. The advantage of this method is that it can define the exact energy range of localized states contributing to the GB–DDLTS signal and avoid the interaction from the other states [15]. With the increase of filling pulse bias, the quasi-Fermi level at the GB shifts gradually from deep states to shallower ones, so the subtracted spectra in figure 4 actually represent the signal of GB states within the energy range defined by two quasi-Fermi levels at the corresponding pulse biases. It can be seen that four trap levels (H1–4) have been revealed by the GB–DDLTS spectra in figure 4. In order to obtain the electrical parameters of GB states related to these traps (H1–4), the Arrhenius plots of $\ln(e/T^2) \sim 1/T$ have been obtained according to equation (2) by determining the temperature positions of peak maxima under different rate window settings for each trap, as
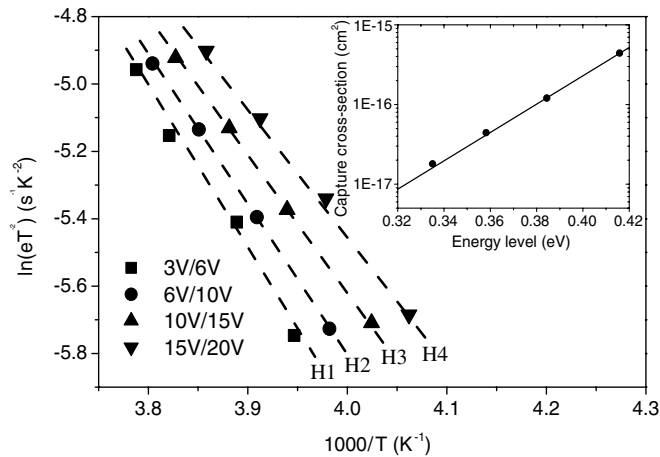
Figure 5. The Arrhenius plots for the four trap states (H1–H4) in figure 3. The inset is the energy position of H1–H4 and the corresponding hole capture cross-sections.

shown in figure 5. The inset gives the energy positions of traps H1–4 and the corresponding hole capture cross-sections. Note that the energy levels revealed by these subtracted spectra are $E_v + 0.34 \sim 0.42$ eV. The corresponding hole capture cross-sections are in the order of 10^{-17}–10^{-16} cm^2, which decreases with their decreasing energy. Obviously, such hole capture cross-sections of GB states result from the Coulomb repulsion of free holes from the charged GB, which suggests a sufficiently large GB state density in the present sample. It should be mentioned that in some error exists the electrical parameters of the GB states obtained from the Arrhenius plot due to the difficulty of accurately determining the temperature position of the DLTS broad peak associated with the extended defects. Usually, an alternative way of obtaining the carrier capture cross-section of states related to extended defects is to directly analyze the capture kinetics of states if the density of free carriers at the extended defects is known, i.e. the DLTS signal as a function of the filling pulse width. However, for the GB states distributed at one GB plane, the GB charge density always increases during the short pulse refilling process before reaching the equilibrium state. This results in that the band bending at the GB is not constant and therefore the current density through the GB cannot be well defined. Thus, this method is quite difficult to apply for the GB case.

In order to judge the reliability of the GB energy levels obtained by the Arrhenius plot in figure 5, we compare them with the results of *I–V* deconvolution. According to thermionic emission theory [11], the hole current density (j) flowing across the GB can be expressed by

$$j = A^* T^2 \{ \exp(-\phi_1/kT) - \exp[-(\phi_1 + qV)/kT] \}, \quad (3)$$

where A^* is the effective hole Richardson constant; ϕ_1 is the energy barrier for a hole in gold contact to cross the GB; q is the hole charge; k is the Boltzmann constant and T is the absolute temperature. The value ϕ_1 is actually equivalent to quasi-Fermi level for holes at the GB under the equilibrium state. Figure 6 shows the quasi-Fermi levels at different biases by deconvoluting the *I–V* curve as well as the energy positions
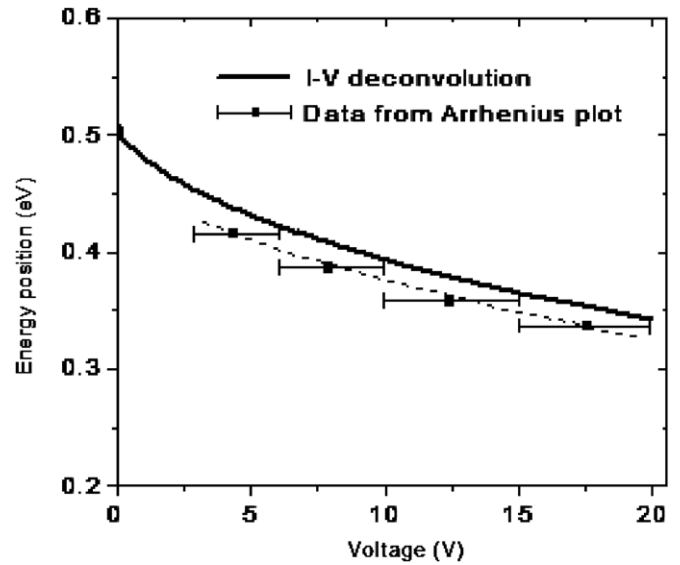

Figure 6. The energy position of the quasi-Fermi level at the GB as a function of bias voltage by *I–V* deconvolution and the energy positions determined by Arrhenius plots.

of GB states determined from Arrhenius plots. It can be seen that the values obtained by the Arrhenius plots are quite close to the energy range defined by quasi-Fermi levels at the corresponding pulse voltages. This suggests the present signature of GB states obtained from the Arrhenius plots of subtracted DLTS spectra is basically believable.

In conclusion, we have clarified that the GB states at the clean large angle (1 1 0)/(1 0 0) GB are localized. Meanwhile, the GB–DLTS signal has been well understood and the peak in the spectrum is not appropriate for determining the electrical parameters of these states, due to the hole capture involved in the maximum signal. A new method of subtracting spectra obtained under various pulse voltages has been applied to define the signature of the relatively shallower localized GB states. Their energy levels are in the range $E_v + 0.34 - 0.42$ eV with hole capture cross-sections of 10^{-17}–10^{-16} cm^2. Since the present shallow (1 1 0)/(1 0 0) GB is rather clean after a controlled high temperature annealing to out-diffuse the interfacial impurities, the main interfacial defects are believed to be the intrinsic distorted structure. Accordingly, the energy levels revealed here are likely to be distorted bond related.

Acknowledgment

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