Evidence for the Improved Defect-Pool Model for Gap States in Amorphous Silicon from Charge DLTS Experiments on Undoped *a*-Si:H

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Results of the first charge deep level transient spectroscopy (DLTS) measurements on undoped *a*-Si:H are presented. The ability of the charge DLTS technique to resolve the gap-state distribution and to monitor directly its evolution after preequilibrium preparation by bias annealing is demonstrated. Three groups of gap states with mean energies of 0.63, 0.82, and 1.25 eV are observed. The condition for their creation as well as the energy values are in a good agreement with the D^+, D^0, and D^- states of the improved defect-pool model. [S0031-9007(97)02393-4]

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The deep level transient spectroscopy (DLTS) is a powerful method not only for the identification of deep levels in crystalline semiconductors but also for studying gap states in amorphous silicon [1,2]. The authors give a rigorous analysis of the relationship between the density of gap states $g(E)$ and DLTS spectra. The analysis and the performed experiments show that the DLTS spectrum is extremely sensitive to changes in $g(E)$, and raw DLTS data are in a form which is very close to the shape of $g(E)$. However, the application of the original capacitance method to *a*-Si:H requires a low frequency (1–100 kHz) capacitance meter instead of the 1–20 MHz capacitance meter typical of most DLTS systems. A low measurement frequency is necessary to make the dielectric response turn-on temperature low enough to observe the gap states over an appreciable fraction of the gap. In other words, the assumption of the capacitance DLTS to be fulfilled, i.e., the relaxation processes of carriers in the gap states within the depletion region are monitored through the changes of the depletion region capacitance. This limits the application of the capacitance DLTS only to doped *a*-Si:H. From this point of view, the current version is preferable, because direct detection of the thermally excited electrons in the form of current in the external circuit has no such limitation. The advantage of using current transients over capacitance ones is also evident at low temperatures because the lowest temperature in the former case is limited only by the rate window setting. Nevertheless, the loss of signal amplitude with increasing time constant τ of the transient, considerable influence of the leakage current and higher relative sensitivity to interface states make the current DLTS of little use. These shortcomings can be suppressed, and the direct detection of the released charge can be utilized for the investigation of high resistivity semiconductors, e.g., undoped hydrogenated amorphous silicon (*a*-Si:H). The first shortcoming is successfully removed by the charge DLTS (Q-DLTS) [3], where the current transient is integrated, yielding a charge transient. This integration eliminates the τ^{-1} amplitude loss and makes the charge sensitivity independent of the time constant τ. The Q-DLTS spectrum is sensitive to the leakage current if the charge integrated due to this current during measuring time is comparable with the transient charge. This parasitic charge, which usually increases exponentially with temperature, causes a shift of the base line of the Q-DLTS spectrum. Then, the existing peaks are superimposed on such an exponential tail. To prevent this situation, the leakage current of our diodes under test was reduced via an additional treatment of the *a*-Si:H surface before Schottky barrier preparation. Bombardment of the *a*-Si:H surface with Ar atoms of energy of 300 eV for 7 min creates a very thin (≈20 nm) semi-insulating layer. This decreases the leakage current below 10^{-8} A even at a temperature of 450 K and makes the leakage current negligible in the whole temperature range of measurements. Thus, after gold evaporation onto the pretreated *a*-Si:H surface, we have obtained metal-insulator-semiconductor- (MIS-) like structure. The films of *a*-Si:H with a thickness of 1 μm were deposited on n^+ *c*-Si substrates by glow discharge decomposition of undiluted silane at the usual deposition conditions. The bulk Fermi level position E_f of these films was determined from the activation energy of the dc conductance at the forward bias of Schottky diodes without the above mentioned treatment of the *a*-Si:H surface. The typical value of the Fermi level position referring to the conduction level E_c was 0.69 eV.

We add a short comment on the time-domain capacitance measurement. This kind of capacitance, based on the feedback charge *C-V* (capacitance versus voltage) technique published by Mego [4], was used because there is a direct connection to the Q-DLTS. The time-domain capacitance is defined as a ratio of the charge $q(t)$ integrated by the charge sensitive amplifier at the point in time t after the end of the probing pulse, δU and the amplitude of this pulse,

$$C_x(t) = \frac{\Delta q(t)}{\delta U} = \frac{\Delta u(t) C_F}{\delta U}, \qquad (1)$$

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where $\Delta u(t)$ and C_F are the output voltage and the feedback capacitance of the charge amplifier, respectively. Thurzo and Grendel [5] generalized Mego's approach and found a relation between $C_x(t)$ and the capacitance $C(\omega)$ measured usually by a sinusoidal voltage. The shift of the sampling time t to longer times corresponds to lower frequencies and vice versa. For the definition of low and high frequency capacitances, the ratio t/τ is crucial, where τ represents the time constant of a particular relaxation process in the sample.

In this paper we report the changes in the gap-state distribution due to different defect chemical potentials at the equilibration temperature $T^* = 490$ K observed by the Q-DLTS. As a matter of fact, our Q-DLTS measurements follow the experiment suggested by Winer [6] to test his defect-pool model which was further developed by Powel and Deane [7]. The main conclusion of this model lies in resolving the apparent contradiction between electron-spin resonance data, which require a positive correlation energy U, and equilibrium gap-state spectra, which show D^- in n-type a-Si:H to lie below D^0 in undoped a-Si:H, as might be expected for negative-U defects with fixed defect energies. The idea of the experiment is to shift the Fermi level of an equilibrated a-Si:H film in a MIS sandwich by a bias voltage, and to monitor the resulting change in the defect distribution as the film re-equilibrates. Since the defect chemical potential depends on the Fermi energy, such a shift of the Fermi level at the equilibration temperature should change the proportions among the concentration of the components D^+, D^0, and D^- of the density of states [7]. In the following we present the results of our observation of these changes through the direct detection of thermally released charges from these states below the equilibrium temperature. The time-domain capacitance versus bias voltage curves of the sample under investigation at a temperature of 450 K is shown in Fig. 1. We can recognize the typical features of a MIS structure capacitance on a n-type semiconductor. At the forward bias the curve reaches the accumulation capacitance of 1800 pF while under the reverse bias the capacitance decreases to 60 pF. The former value corresponds to the 22 nm thick semi-insulating layer created during the Ar bombardment, and the latter capacitance corresponds to the width of the a-Si:H layer. A more detailed comment on both the observed hysteresis and the particular C-V curves in Fig. 1 will be given after the discussion of Q-DLTS spectra. The main results of the Q-DLTS experiments are summarized in Fig. 2. All the spectra were obtained with the same measurement parameters: bias voltage $U_b = -3$ V, excitation pulse $\Delta U = +3$ V, and rate window 50 s^{-1}. The spectra differ only in the respective bias voltages U_{ba} applied during the sample annealing at a temperature of 490 K for 10 min to reach an equilibrium state. The spectra reflect changes of the defect distribution in undoped a-Si:H due to shifting the Fermi level of an equilibrated

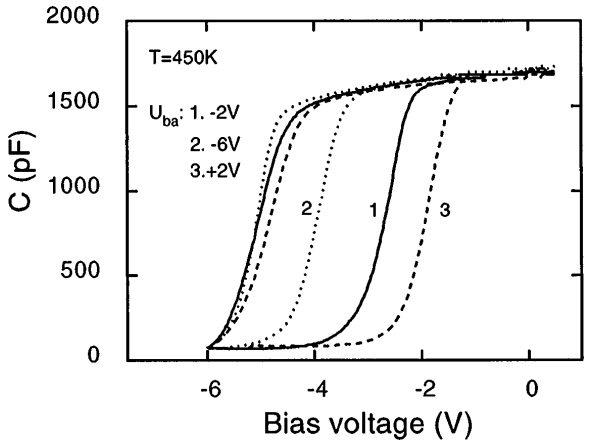

FIG. 1. Capacitance versus voltage dependences of a Schottky barrier on undoped a-Si:H, where top gold electrodes were evaporated after the bombardment of a-Si:H surface by Ar atoms. The parameter of the curves is the bias voltage U_{ba} applied during the sample annealing at the equilibrium temperature of 490 K for 10 min to create different equilibrium distributions of defect states.

a-Si:H layer through U_{ba}. Let us focus on spectrum 1 in Fig. 2, measured after the annealing at $U_{ba} = -2$ V. At first glance, we can recognize three peaks in the spectrum, positioned at 320, 390, and 430 K. When the sample is annealed at $U_{ba} = -6$ V and $+2$ V before measurement, the Q-DLTS spectra are dominated by peaks at 320 K (spectrum 2) and 430 K (spectrum 3), respectively. Activation energies of these two distinct peaks, as determined from respective Arrhenius plots, are 0.63 eV for the peak at 320 K and 1.25 eV for the peak at 430 K. According to the defect-pool model, the shift

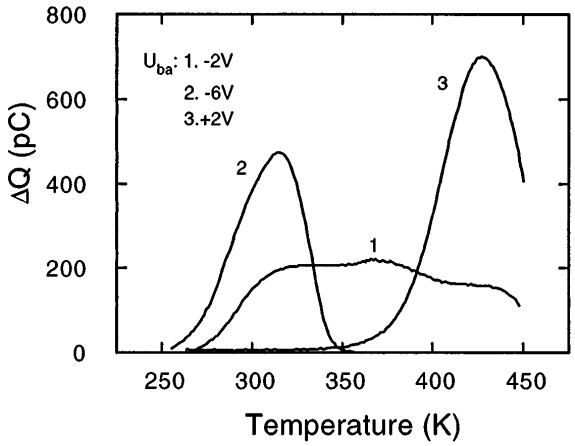

FIG. 2. The Q-DLTS spectra of the undoped a-Si:H annealed at different U_{ba} and equilibrium temperature of 490 K for 10 min. The spectra were measured with $U_b = -3$ V bias voltage, pulses to 0 V and rate window of 50 s^{-1}. The energies of the defect states at the peak maxima 2 and 3 are 0.63 and 1.25 eV, respectively.

of the Fermi level with the applied bias U_{ba} changes the defect potential and creates a condition for a new equilibrium distribution of the density of states. It means that the bias annealing at $U_{ba} = -6$ V and $+2$ V at the equilibration temperature fulfills conditions for the creation of D^+ and D^- components, respectively. Therefore, we identify the peak at 320 K with D^+ and the peak at 430 K with D^- components of the density of states. Agreement of the experimentally obtained energies with the expected ones supports our assumption. Considering this, we performed an experiment to determine the parameters of the middle component in spectrum 1. The sample was annealed at 490 K with $U_{ba} = +0.5$ V for 10 min, and the measurement was carried out at $U_b = -0.6$ V with excitation pulses of 0.6 V. The applied U_{ba} suppressed the creation of D^+ states, and the measurement conditions did not allow the D^- states to respond (Fig. 3). The activation energy of this peak determined from an Arrhenius plot is 0.82 eV, again in good agreement with the localization of the D^0 component in the gap. It should be noted that the above mentioned annealing treatments are reversible. A further important experimental finding is related to the frequency factor ν_0 of the Q-DLTS peak maxima which successively increases from 8×10^{11} s^{-1} for 0.63 eV, 3×10^{12} s^{-1} for 0.82 eV to 2×10^{16} s^{-1} for 1.25 eV. According to a recent report [8], this fact points to an energy dependence of the frequency factor in a-Si:H. This kind of dependence is known as the Meyer-Neldel rule and seems to be a significant phenomenon in a-Si:H [9].

Now, we propose the following explanation for the shift of the C-V curves after the sample annealing at different biases. Unlike a standard MIS structure, it is not connected with the charge trapping at the semiconductor/insulator interface, which should cause a shift of the flat band voltage. In our case, in undoped a-Si:H there is no shallow dopant level supplying the semiconductor with free carriers. Such carriers are available only from the conductance band tail, and the density of states and therefore the shapes of the C-V curves are determined by these carriers. As was found in the Q-DLTS measurements, annealing at $+2$ V led to the creation density of states with energies at about 1.25 eV, which means that the thermal emission time constant is approximately 1.5 ms at 450 K. The sampling time t for the time-domain capacitance measurements was set to 300 μs and represents a demarcation delay for thermally emitted carriers to contribute to the measured signal. Thus, after depletion of electrons from the conductance band tail, the capacitance starts to decrease at -2 V toward its minimum value of 60 pF (curve 3). A proportional distribution of the density of states among the three groups of defects after a bias annealing at -2 V is reflected in the C-V curve as a shift of the capacitance decrease to more negative biases (curve 1). The mean time constants of electrons emitted from D^+, D^0, and D^- centers are approximately 14 μs, 500 μs, and 1.5 ms, respectively, and the density of states are able to supply charge carriers up to the moment when all states with sufficiently short time constants with respect to the sampling time t are empty. The capacitance decrease is shifted to the highest reverse bias (curve 2) when the defect states with the mean time constant of 14 μs are dominant. Because of the semi-insulating layer, a generation of free carriers via gap states is also present. It is observed in the form of a capacitance increase with the change of the direction of the sweeping bias. The rates of the carrier generation for particular states of the sample, as given by the bias annealing, were compared in measurements of the time dependence of the capacitance at a constant bias of -6 V. Its gradual increase is connected with the creation of an inversion layer at the a-Si:H/semi-insulating a-Si:H interface. These dependences are shown in Fig. 4. The changes of the gap states of a-Si:H also influence the rate of the inverse layer creation in the undoped a-Si:H based MIS-like structure. The fastest generation rate is found in the case when the component D^+ dominates the defect states. On the other hand, the slowest rate characterizes the situation when the D^- component is dominant. This is convincing evidence that the time constant of the carrier generation is determined primarily by the emission of electrons from the gap states to the conduction band.

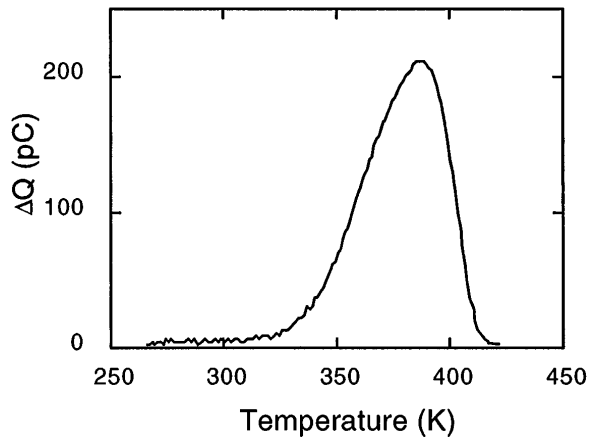

FIG. 3. The middle part of the Q-DLTS spectrum 1 from Fig. 2. is shown. The separation was achieved using the following conditions: sample annealing at $U_{ba} = +0.5$ V and 490 K for 10 min, $U_b = -0.6$ V, pulses to 0 V, rate window of 50 s^{-1}. The energy at the peak maximum is 0.82 eV.

In conclusion, the results of the Q-DLTS measurements on undoped a-Si:H are presented for the first time. We observed three groups of the gap states with mean energies of 0.63, 0.82, and 1.25 eV. The conditions for their creation as well as the energy values are in good agreement with the improved defect-pool model. The new surface treatment before Schottky contact evaporation implies further possibilities for Q-DLTS experiments on undoped a-Si:H. A promising experiment would be the

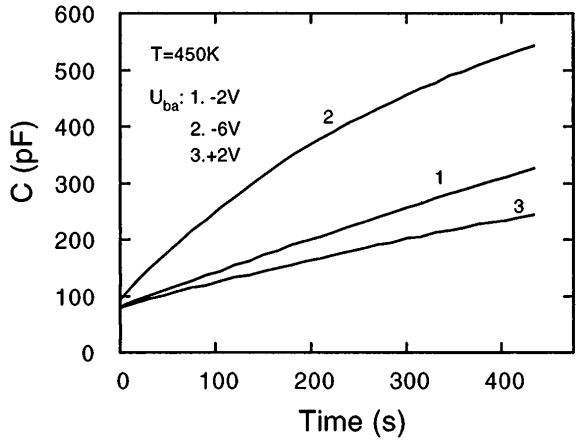

FIG. 4. The capacitance of the undoped a-Si:H based MIS-like structure annealed at different U_{ba} as a function of time. The reverse bias was kept at -6 V.

monitoring of the density of states after a light soaking and correlation with results of other techniques, especially electron paramagnetic resonance, used in this field. In addition, challenging for the future is the application of the Q-DLTS technique for the investigation of other undoped and semi-insulating materials such as a-Ge:H, high purity crystalline silicon, and semi-insulating GaAs.

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