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Observation of time-varying photoconductivity and persistent photoconductivity in porous silicon

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We have observed time-varying photoconductivity and persistent photoconductivity in porous silicon, both with time-evolution scales of the order of several minutes or hours. The time evolutions depend on the wavelength and the intensity of the illuminating light. The data indicate the presence of at least two competing mechanisms, one is tentatively related to photoinduced creation of charge carriers in the silicon substrate followed by diffusion into the porous silicon layer, and the other is tentatively related to desorption of hydrogen from the porous silicon. © *1996 American Institute of Physics.* [S0021-8979(96)99902-2]

I. INTRODUCTION

Silicon, which has been anodically etched in hydrofluoric acid [so-called porous silicon (PS)], has attracted a great deal of interest in the last few years, because of its bright visible luminescence, which is in clear contrast to the very poor luminescence of pure, crystalline silicon (*c*-Si). For reviews with references to previous works, see, e.g., Refs. 1–3. Emission properties of PS have been studied in detail,[1–3] especially with the use of photoluminescence (PL), photoluminescence excitation (PLE), and also with other emission techniques like electroluminescence.[3,4] Absorption processes in PS, on the other hand, have not been studied nearly as much. This is probably because direct observation of photoabsorption is hampered by the absorption taking place in the *c*-Si substrate.

We have undertaken a systematic study of PS by combining PL and PLE with photoconductivity (PC), which is based on photoabsorption and may thus yield information about absorption properties of PS. In the course of this, we have observed time-varying PC and also persistent photoconductivity (PPC), both with characteristic time scales of the order of minutes or hours, which we report and discuss in the following.

II. EXPERIMENT

The samples were prepared by anodically etching of *p*-type silicon in HF, using a standard technique similar to that described, e.g., in Ref. 5. Sample surfaces etched to different degrees yielded similar results. After etching, the samples were mounted strain-free on holders, and electric contacts to the PS layer were formed by flat metal spring leaves, which were strong enough to create durable contacts, but so soft that the PS layer they touched was not damaged. The separation between the two contacts was a few millimeters, and all data reported here have been obtained with a potential drop of 5 V between the two contacts, so that the overall electric field strength was around 2 V per millimeter. As illumination, a 250 W halogen lamp coupled to a monochromator (McPherson model 207) was used, different spectral orders being separated by appropriate filters. At the exit slit of the monochromator a bifurcated optical fiber cable was mounted in such a way that the sample could be illuminated by one of the cable outputs, while the other output was coupled to an optical power meter, so that the illumination of the sample could be monitored continuously without interrupting illumination of the sample. The short-wavelength limit, 400 nm, used in this work, was set by absorption in the glass fibers below this wavelength. All data reported here have been taken at room temperature.

The samples were stored in darkness, and the dark current was recorded continuously. In all of the measurements reported here, the illumination was not carried out until the dark current had stabilized entirely, to ensure that one series of measurements was unaffected by the previous ones.

III. RESULTS AND DISCUSSION

Figure 1 shows typical current versus time curves obtained with one and the same sample. For all of the curves in this figure, the time at which illumination of the sample was initiated, has been set equal to zero, and the time at which the illumination was terminated, has been marked with a vertical arrow. The curves are labeled with the wavelength of the illuminating light. For each curve, a prompt increase in the current is seen at the beginning of the illumination, and the height of this step in the signal is marked with a horizontal arrow at time $t=0$ for each curve. The time scale of this prompt increase was less than a few milliseconds, the time resolution being limited by the experimental setup. The height of the prompt step is more easily seen in Fig. 2, which shows the time evolution for selected curves from Fig. 1 the first few minutes after illumination was initiated. Corresponding measurements on *c*-Si revealed nothing but prompt jumps, as expected, again with time resolution set by the experimental setup.

Besides the prompt changes observed for $t=0$, slow changes, having time scales of the order of several minutes or hours are also seen in Fig. 1. For all of the curves given in

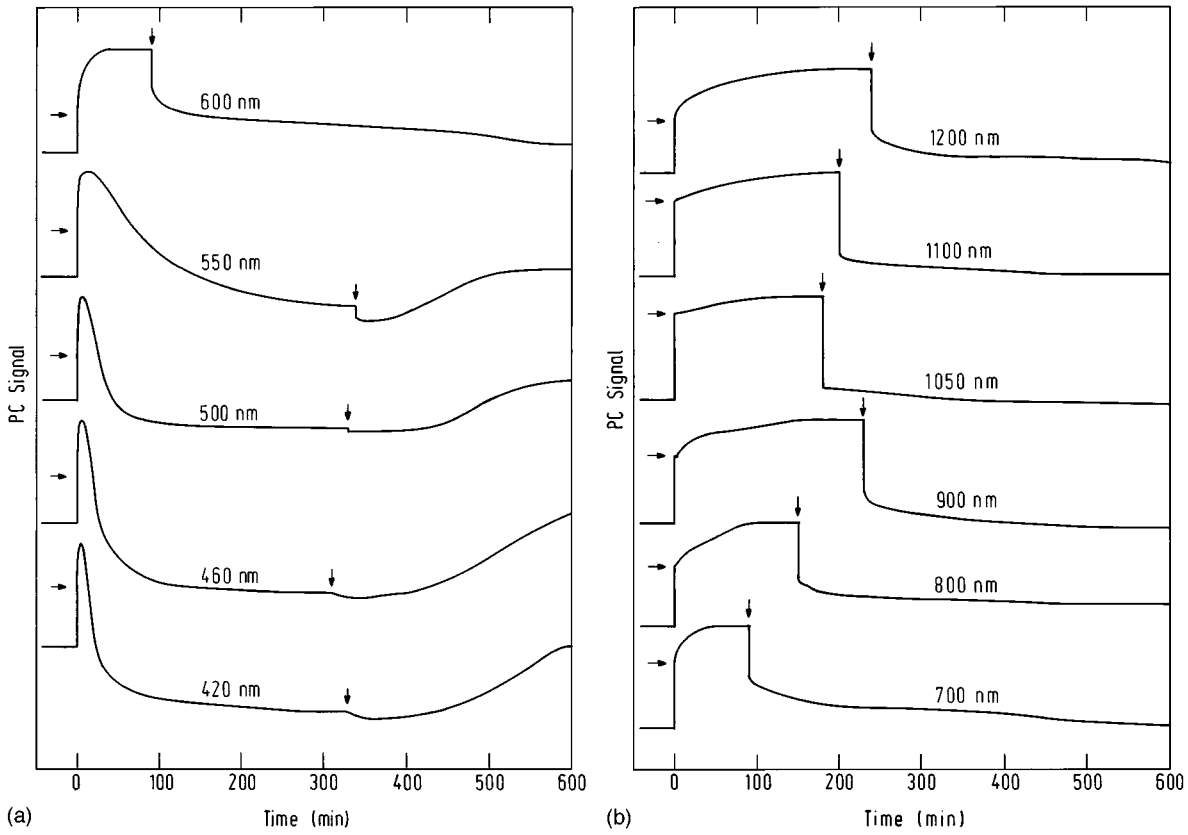

FIG. 1. (a) The figure shows PC and PPC for one sample, obtained with different wavelengths of the illuminating light in the interval 420–600 nm, as indicated for each curve. For each curve, the illumination was initiated at time $t=0$, the height of the prompt increase in current at $t=0$ is shown with a horizontal arrow, and termination of the illumination is indicated with a vertical arrow. The curves have been displaced vertically to avoid overlaps, but the initial dark currents were at the same level. The curves have been normalized to show the same maximum PC signal. (b) The figure shows PC and PPC for the same sample as that used for (a), obtained with different wavelengths of the illuminating light in the interval 700–1200 nm, as indicated for each curve.

Fig. 1, the illumination was not interrupted until the current through the sample had stabilized. From Fig. 1, we note the following.

(i) For wavelengths above approximately 1200 nm, no PC is observed. This corresponds to the well-established photoconductivity response of pure silicon, cf. Ref. 6. Thus, this finding is no surprise!

(ii) For wavelengths below $\simeq$1200 nm but above $\simeq$600 nm [Fig. 1(b)], the current increases slowly and monotonically in time during illumination until finally a stable level is reached. Correspondingly, the PPC signal shows a similar decrease in time. The time to reach a constant, illumination-induced current tends to increase with increasing wavelength.

(iii) For wavelengths in the interval $\simeq$400–600 nm [Fig. 1(a)], the PC first increases in time, but reaches a maximum value in a fairly short time ($\simeq$5–10 min) and then, it decreases and stabilizes finally at a level which is even below the initial dark current level. This is the most interesting finding of our work. After the illumination is switched off, the PPC first decreases slightly further, then passes through a minimum whereupon it slowly increases monotonically, and the initial dark current level is reached only after several hours of darkness.

(iv) For wavelengths above approximately 600 nm, the prompt increase in PC observed at $t=0$ equals the prompt decrease in current observed when the illumination is turned off. However, for shorter wavelengths, the prompt increase at $t=0$ is much larger than the prompt decrease, the latter being barely discernible.

With a pure *c*-Si sample, we naturally observed finding (i), but none of the findings (ii)–(iv). The above-listed findings were found to be reproducible not only from day to day, but also over periods of several weeks.

In Fig. 3 PC signals versus wavelength of the illuminating light for pure *c*-Si (bottom curve) as well as for four different PS samples are plotted. In all cases, each spectrum was recorded during a time which was short in comparison to the times which are characteristic for the processes described above. Thus the curves in Fig. 3 mainly present the prompt PC signals in comparison to that for pure silicon. Clearly, the five curves presented in Fig. 3 have thresholds at the same wavelength, namely at approximately 1200 nm, in close agreement with (i). Also there is a close resemblance between the five curves from threshold and down to approximately 1100 nm, where the PC signal obtained with the pure *c*-Si sample passes through a maximum, in agreement with well-established results, see, e.g., Ref. 6. However, for

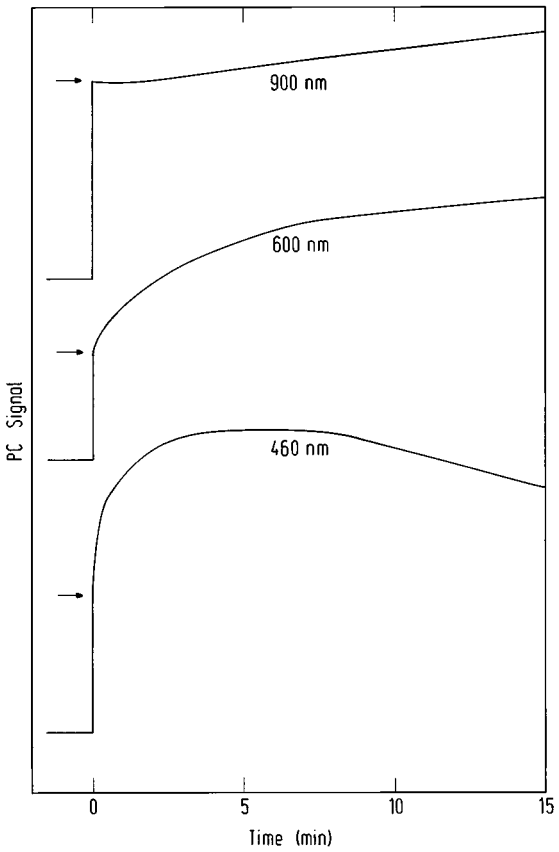

FIG. 2. Selected curves from Fig. 1 are shown here on a different time scale in order to show more clearly the height of the prompt signal and the time development immediately after illumination has been initiated.

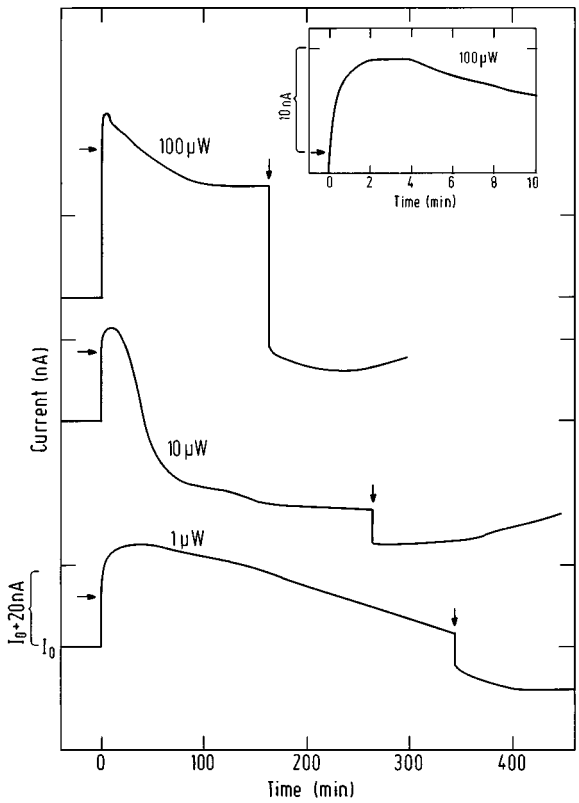

FIG. 4. The figure shows PC and PPC for one sample obtained with three different illumination intensities of a 544 nm wavelength. The horizontal arrows at time $t=0$ indicate the heights of the prompt increases in PC and the vertical arrows indicate the time at which the illumination was switched off. The insert shows the evolution of the curve obtained with illumination power equal to 100 μW, during the first 10 min of illumination.

shorter wavelengths, the PC signal from the *c*-Si sample decreases steadily and is very small below $\simeq$900 nm, which is well established for *c*-Si.[6] In contrast to this, the PC signal from the four PS samples have maximum values at approximately 950 nm, and they have short-wavelength tails which extend all the way down to the shortest wavelengths used by us. These tails clearly surpass that seen for *c*-Si. In our corresponding PL spectra, we observed a broad spectral feature with a maximum around approximately 720 nm, which is somewhat below the maxima of the four PC curves for PS in Fig. 3.

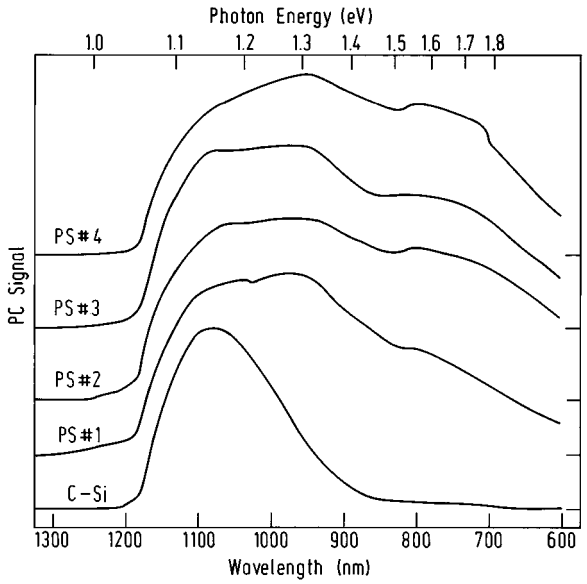

FIG. 3. Photoconductivities for four porous silicon samples and a pure *c*-Si sample (bottom curve) plotted as functions of the wavelength of the illuminating light.

In Fig. 4 PC signals obtained with one sample at three different illumination intensities of a 544 nm wavelength are shown. For this purpose, a green HeNe laser was applied. From the figure is seen, that the higher the illumination power, the faster the time evolution, but neither the magnitude of the prompt signal nor that of the time-dependent PC signal are proportional to the incoming photon flux. Similar features were observed with other excitation wavelengths.

For pure *c*-Si, data like those presented above have not been reported. For amorphous hydrogenated silicon and also for modulation-doped silicon-based superlattices, PPC has been reported and interpreted in terms of metastable defects created during illumination, see e.g., Refs. 7–9. However, such light-induced conductivity changes are much larger than what we observe and also, the time-evolution scales differ from ours. Thus the interpretations given in e.g., Refs. 7 and 8 cannot be taken over here without modifications. We mention that the thickness of the porous silicon layer used by

us was substantially smaller than the thickness of amorphous silicon used by others. Thus a possible content of amorphous silicon in our sample was much below the corresponding layer thickness of amorphous silicon used, e.g., in Refs. 7 and 8. This in itself will introduce a marked difference which in any case has to be taken into account when interpreting our data.

The time scales of minutes or even hours for the evolutions shown in Figs. 1 and 4 are so long that they indicate presence of one or more diffusion processes. We have unsuccessfully tried to rationalize all findings with the use of only one diffusion process. Rather, the change in curve shape seen around approximately 550 nm, cf. findings (ii) and (iii) listed above, shows that at least two different and competing processes are active, one of them leading to an increase in the PC, and the other one reducing the PC. The latter is only active for wavelengths shorter than approximately 550 nm (2.25 eV). In the following, we shall discuss these two features one at a time. For the mechanism leading to an increase in PC, we notice that it is active for all energies above the photoconductivity band gap of *c*-Si. This indicates that it is at least partially related to creation of electron-hole carriers in *c*-Si, and as seen from Figs. 1 and 2, the shorter the excitation wavelength, the faster the time evolution will be. From Fig. 4 is seen that the time evolution runs faster with increasing density of carriers in the PS layer, and this can explain the above-mentioned wavelength dependence of the time evolution, because the absorption coefficient in PS decreases steadily with increasing wavelength.[10] Therefore, for short wavelengths, most or all excitation takes place in the porous layer, with a high density of photocreated carriers there as a result, and with increasing wavelength, the density of photocreated carriers in the PS layer will decrease at the same time as more and more carriers will be created in the unetched silicon. These can subsequently diffuse into the porous silicon layer, where their presence leads to creation of metastable defects that entrap carriers, preventing recombination with carriers of opposite sign and thereby enhancing the conductivity.

We are not able to say exactly what microscopic mechanism is involved in the creation of metastable defects. We mention that for amorphous silicon, such defects can be created by a variety of different means, including illumination, electric currents and electric fields, and these experimental results are quantitatively consistent with a model that involves diffusion of hydrogen.[11] Thus a similar model involving hydrogen diffusion in the creation of metastable defects may be applicable to our data as well.

The other mechanism mentioned above is active only for wavelengths shorter than approximately 550 nm. Again, we are not able from our data to point out one single mechanism as being responsible for the decrease in PC. A plausible explanation could be, that the PC quenching is related to photochemically induced desorption of hydrogen atoms from the surface of the etched silicon. Photoinduced loss of hydrogen from porous silicon has been observed for photon energies near 3 eV,[12] with a rapid increase of the desorption rate when the photon energy exceeds 3 eV. In Ref. 12, the authors report hydrogen desorption for photon energies down to below 2.8 eV, and they show that the desorption rate is strongly sample dependent. This is compatible with the threshold energy around 2.25 eV that we observe. The desorption will increase the number of dangling bonds on the hydrogen-passivated surface, which leads to enhanced recombination at the surface. Because of the very large surface of PS, a marked reduction of the conductivity would be expected. For the shorter wavelengths, the excitation will take place near the surface according to the discussion above. One would thus expect that an enhanced surface recombination would strongly reduce the PC for the shortest wavelengths, and this is exactly what we observe, see (iv). The reduction of the prompt signal after several hours of illumination with short wavelengths is thus fully consistent with an increase of the surface recombination.

To investigate this mechanism further, a sample was lacquered with an ordinary transparent lackspray. The sample was illuminated with 450 nm light before and after the lacquering, and the time-varying PC signal was recorded. The shape of the PC signal was the same as before, see Fig. 1(a), but the time used to reach a minimum was increased by more than a factor of 10. This is consistent with hydrogen desorption from the surface, where the transparent lack covering the surface will make the hydrogen desorption more difficult. However, as mentioned above, this interpretation is speculative, and further investigations are needed in order to confirm or reject it.

In addition to the major trends, as listed and discussed above, we mention an additional observation. With light in the wavelength region=700–1000 nm, the slowly varying PC showed a small decrease in the early stage of the light being switched on, with total duration of less than 10 min, see the curve labeled ''900 nm'' in Fig. 2. A corresponding small increase in the dark current was observed right after the illumination was terminated. Both of these small variations in the signal may be traces of the effect observed by Staebler and Wronski[13] for amorphous silicon; namely, that the optical exposure increases the density of gap states, and such an introduction of new gap states can lead to shorter electron lifetimes, which in turn will produce a lowering of the PC. This Staebler–Wronski effect[13] is, however, in our work a minor detail and cannot explain our main findings, (ii)–(iv) given above.

Porous silicon has been found to be a highly sensitive photodetector.[14,15] Our observation of time-varying PC and PPC with time scales as shown in Figs. 1 and 4 implies restrictions on the use of PS for photodetection.

IV. SUMMARY

In conclusion, we have observed time-varying PC and persistent PC in porous silicon, both with time scales of several minutes or hours. The time evolutions depend in a complex way on the wavelength and the intensity of the illuminating light. At least two different competing mechanisms are observed, one is tentatively related to photoinduced creation of charge carriers in the silicon substrate followed by diffusion into the porous layer. The other, observed only for shorter wavelengths, is tentatively related to photoinduced hydrogen desorption from the porous silicon.

ACKNOWLEDGMENTS

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