Observation of a saturation of optical absorption in porous silicon

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(Submitted 11 April 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **59**, No. 10, 678–681 (25 May 1994)

A saturation of the optical absorption has been observed in thin, transparent layers of porous silicon. This saturation is "remembered." The effect is shown to be similar in its manifestations to the "fatigue" of luminescence which has been reported previously. It is probably the main reason for this fatigue.

The original model of porous silicon assumed that the optical properties of this material were governed by exciton processes in a 3D conglomerate of quasi-1D silicon quantum wires.[1] However, research on this unusual material generated more and more results whose explanation required a more elaborate model and the introduction of some further assumptions. Among these assumptions are a "fatigue" or "photodegradation" of luminescence—an effect which had been seen even in the first studies of porous silicon.[2] In a study[3] devoted to this effect, it was attributed to the existence of some special bistable centers which serve as centers of nonradiative recombination, with the energy coming from a localization of carriers. Chang *et al.*[3] adopted, with minimal changes, the model which had been used to explain the luminescence fatigue of hydrogenated amorphous silicon[4] and, earlier, that of some other semiconductors.[5]

However, this model fails to explain why the fatigue is clearly noticeable during excitation of the luminescence by visible-range lasers (488 and 633 nm), while the effect is seen only faintly during excitation by nitrogen or excimer lasers (337 and 308 nm). We have suggested that the dependence of the effect on the photon energy of the exciting light indicates that the luminescence fatigue is actually a manifestation of unknown (in the case of porous silicon) processes which involve a change in the absorption of light. These processes might be similar in nature to those which lead to the familiar burning of spectral holes.[6] The situation which prevails during the excitation of luminescence, with states of one fixed excitation energy being excited, and with recombination occurring in a set of other states (at other wavelengths), may promote the depletion of absorbing states. The difference between the results of experiments using visible and UV excitation of the luminescence can be explained quite easily in the following way, for example. As the luminescence is excited by a photon with the larger energy, the absorption occurs predominantly to states of a band type (delocalized states), and the "memory" of the excitation event is erased in the course of thermalization. During excitation by light with the lower photon energy, the excitation occurs in the region of localized states. In turn, since the lifetime of the excited carriers at local centers may be fairly long, the result may be that centers with a certain excitation energy may become "disconnected" from the absorption. Since the material which has been studied is fairly nonuniform, it is completely possible that there is, on the average, no sharp boundary between localized and delocalized states.

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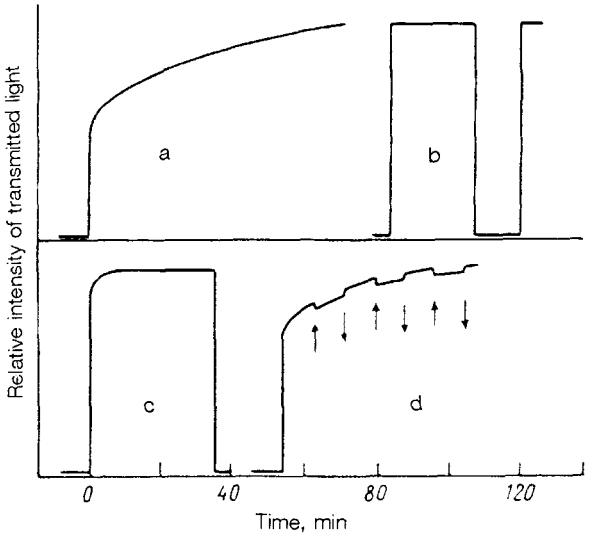

FIG. 1. Evolution of the intensity I of the beam from the He–Ne laser (633 nm) after passage through a sample of porous silicon. The curves have been normalized to their maximum value along the ordinate. a—First illumination; b—subsequent illuminations; c—transient process during a repeated illumination, after exposure to UV light; d—partial restoration of the absorption during auxiliary illumination by light at 488 nm. The arrows show the times at which the 488-nm light was turned on and off.

Since the standard samples of porous silicon are opaque and thus unsuitable for absorption experiments, an important part of the present study was to prepare some appropriate samples. For the experiments, we produced samples of porous silicon on a substrate by the standard procedure of anodic etching.[1] Scales of genuine porous silicon, with typical dimensions of $0.2\times0.2\times0.02$ mm, were then mechanically removed under a microscope. These scale samples were cemented with a transparent lacquer to blackened metal diaphragms with a hole of the appropriate diameter. The use of samples of this sort reduced the risk of damage to the sample itself and made it possible to reliably position the light upon the sample. To measure the transmission we used the focused beam from a 30-mW He–Ne laser. The argon laser at our disposal was used only for auxiliary excitation, because of its pronounced intensity instability.

Figure 1 shows some typical experimental results on the evolution of the transmission. After illumination begins, the intensity of the transmitted light initially increases (curve a). After illumination for 30–60 min, no further visible changes occur. Turning the light off for a time interval up to 1–2 days and then turning it back on again lead to the transmission level corresponding to saturated absorption (b in Fig. 1). We might point out that this observation rules out heating as a possible cause of the observed effect.

To find a more detailed picture of the observed absorption saturation, we applied some other agents to a sample with saturated absorption. Part c of Fig. 1 shows the initial region of the evolution of the transmission during a repeated illumination for a sample which had been removed from the beam from the He–Ne laser beforehand, for a time T

on the order of 15 min, and exposed to the focused beam from the nitrogen laser. We see that in this case it is again possible to see a transient region with an increasing intensity of the transmitted light.

Finally, we carried out a two-beam experiment, like that described in Ref. 3 for luminescence. In this experiment we measured the effect of the second beam (488 nm, 30 mW) on the transmission of the probe light from the He–Ne laser. As expected on the basis of our model, we found curve d, which is symmetric with respect to curve 5 in Ref. 3: The absorption of light with a wavelength of 488 nm, in addition to the red light, leads to a decrease in the saturation of the absorption (i.e., to a decrease in the intensity I of the 633-nm light transmitted through the sample).

Unfortunately, we find it difficult to offer a rigorous quantitative characterization of the observed effects. Quantitative measurements were not possible because of two factors: the nonuniformity of the material, which means that the results are not reproducible when we switch from one microscopic sample to another, and the simultaneous (!) irreproducibility due to a memory of the exposure to light for each of the samples.

Figure 1 shows the typical shape of the curves. The maximum observed transmission increase of the type in part a was by a factor of about 2. During the repeated transient process of type c, the increase ranged up to 10%. The effect of the 488-nm light on the transmission at 633 nm was on the order of 5% of the intensity of the transmitted light. The evolution of the saturation of the absorption is not a single-exponential process.

In all its experimental manifestations, the absorption saturation observed by us thus behaves symmetrically with respect to the known fatigue of the luminescence of porous silicon. The transmitted light increases during a first illumination of the sample, while just after a repeated illumination the transmitted light corresponds to the "remembered" value of the transmission. This memory effect lasts at least 1 day in darkness. It is possible to erase the memory (admittedly, in our case we used UV light, while the fatigue was erased in Ref. 2 by heating the sample). The simultaneous application of light at a different wavelength reduces both the absorption saturation and the fatigue effect in Ref. 3. Lacking clearer quantitative results, we will have to content ourselves here with establishing these qualitative new effects. In the analysis we will have to be content with a comparison of the manifestations of luminescence fatigue and absorption saturation.

The opposite effect of the light at the different wavelength is unnatural for the model proposed in Ref. 3. That effect was not explained in that paper, although it was observed. From the standpoint of our own model, the explanation for the effect is obvious: The absorption of light at the different wavelength occurs at centers with a different excitation energy (saturation of the absorption may also arise at this wavelength). Some of the carriers excited by the second beam become delocalized and participate in recombination with centers which have "memorized" the excitation by the first beam. Some of the centers which are removed from a state capable of absorption by the first beam return to their original state. Experimentally, this effect should be seen as both a decrease in the transmission and an increase in the luminescence intensity; this is just what has been observed. Such a mechanism should also account for the restoration of the absorption after the UV illumination.

Taken together, these observations lead to a fairly obvious conclusion: Saturation of

the absorption underlies the luminescence fatigue in porous silicon. In view of the similarity between the fatigue in the material studied by us and that in the materials in which it has been observed previously, there is the possibility that the existing models for luminescence fatigue should be revised, and they should be applied to other materials.

Nevertheless, we cannot completely reduce the effects observed in luminescence fatigue to a saturation of absorption. The first reason is that we have carried out only some purely qualitative observations. They are an insufficient basis for ruling out possible contributions of other mechanisms. Second, in a study of the fatigue we observed some kinetic features of this effect which are not found in papers by other authors. These features are not a consequence of absorption saturation. A joint analysis of these effects, which will make it possible to draw a much more specific picture of recombination processes in porous silicon, will be the subject of another study.

We wish to thank B. P. Zakharchenya for constant interest in this study.

This study was carried out with partial financial support from the Russian Basic Research Foundation (Project Code 93–02–2603).

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Translated by D. Parsons