

INFLUENCE OF γ -IRRADIATION ON PHOTOLUMINESCENCE OF POROUS GERMANIUM OBTAINED BY TREATMENT IN ELECTRIC SPARK DISCHARGE

The porous Ge layers are produced by spark discharge method. The photoluminescence spectra of these layers are compared with ones for porous Ge obtained by stain, chemical and electrochemical etching. There are the data in references that for porous Ge layers obtained by different methods the maximum for photoluminescence spectrum may be localized by two different wavelengths depending on the production procedure. In contrast to it, our spectra consist of both peaks. Using the results of photoluminescence spectra studies, the comparison of aging effects for porous Ge layers produced by different methods was made. The influence of γ -quanta action on photoluminescence spectra of porous Ge layers was studied.

1. Introduction

The discovery of intensive photoluminescence in visible range of spectrum from porous silicon [1] is interesting to search the similar effects in the other semiconductor nanostructures used in electronics. The detection of photoluminescent properties in porous germanium obtained by chemical etching [2] and by anodization [3] gives the basis to search the similar quantum phenomena in the other porous materials and allows to hope for creation of the new optoelectronic devices on the base of these materials. The above-mentioned expectations are also confirmed by the studies in porous silicon carbide [4] and in porous gallium arsenide [5]. However, the low intensity of photoluminescence for these structure hampers their practical application. This fact forces the search for methods to magnify luminescence. One of them is the development of radiating surface that can be easily realized by creation of nanoclusters in different porous structures, which are already known [6–7].

In contrast to porous silicon, only some papers [2, 3, 8–12] are devoted to porous germanium. In our opinion, it may be explained mainly by complexity of its production, by bad reproducibility of material and by lower intensity of photoluminescence in visible range of spectrum comparing to porous silicon. In the above-mentioned papers the samples obtained by different technologies, were treated by various procedures (for example, laser irradiation, thermal annealing, oxidizing on air or in water vapour etc) during investigation. At the same time, the studies of radiative effect on the given nanostructures are practically missed. In present paper we try to make up for this deficiency.

2. Experimental technique

As the initial material, *p*-type germanium wafer with specific resistance $\rho = 30 \Omega \cdot \text{cm}$ was used. We applied the same germanium as material for electrode during the treatment of sample by spark discharge, though it was of little importance [10–11]. The production of porous layers was carried out by the setup consisting of high-voltage source, contact maker and two-coordinate manipulator (fig. 1). The treatment by electric spark discharge up to 20 hours allows to obtain layers of noticeably luminescent porous germanium with diameter of a spot of about 5 mm. Just this size is the minimal to dispense with photon counter. During the process rather thick white scurf of germanium oxide arises on wafer surface, which is necessary to remove periodically to facilitate the formation of porous layer. The growth strength of porous germanium layer allows to remove the referred «coat» mechanically, without any solvent, as it usually takes place, while using chemical etching [2], when porous layer is obtained thin and friable.

The distinctive feature for the treatment by electric spark is that the spark at each subsequent discharge hits in a place with the lower resistance because of porous layer and oxide on sample surface. Thus, the rather uniform layer results in continuous treatment (even at $\sim 100 \mu\text{m}$ of layer thickness). This fact distinguishes favourably the spark

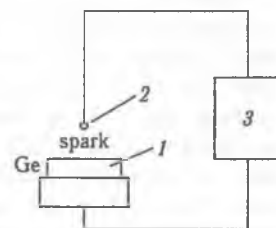


Fig. 1. The scheme of setup to produce porous material by electric spark discharge:

1 — sample; 2 — electrode;
3 — high-voltage source of current

treatment techniques of porous germanium from that obtained by anodization. The investigation of these layers by optical and electronic microscopes (fig. 2, *a* and *b*) specifies the fundamental similarity of porous silicon layers obtained by anodization (fig. 2, *c*).

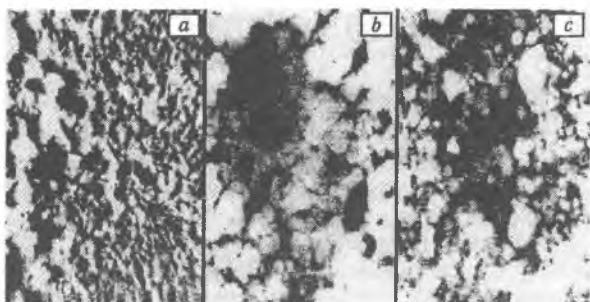


Fig. 2. Photos of porous Ge and porous Si surfaces: *a* — Ge (optical microscope); *b* — Ge (electron microscope); *c* — Si (electron microscope)

The obtained Ge sample with porous layer was exposed to γ -irradiation from ^{60}Co isotope with dose $5 \cdot 10^4 \text{ rad}$. The photoluminescence spectra before and after this irradiation were registered at excitation with ultraviolet laser ILGI-501 (wavelength $\lambda = 337 \text{ nm}$, pulse duration 10 ns , repetition frequency from 10 Hz up to 100 Hz , mean power 25 mW), by the setup consisting of quartz monochromator SF-4, photoelectric multiplier FEU-59, selective amplifier U2-8 and xy-plotter H-307.

3. Results and discussion

As well as in case of porous silicon [13], the distinctive methods to obtain porous germanium layers (and also the different regimes within the same method) lead to the different (and often the opposite) effects. It is noted in [2], that the white thin coating, growing by chemical procedure to obtain porous germanium film and removing in water, results in complete disappearance of luminescence. Thus, the authors [2] make quite valid conclusion that the given thin coating consisted mainly of GeO_2 is responsible for photoluminescence.

Aforesaid, white thin coating of oxide has also appeared when the spark discharge method was used. However, at its subsequent more and more careful mechanical removal, the photoluminescence not only does not disappear, but its intensity, on the contrary, increases without change in shape of spectrum and shift in the peaks (fig. 3).

Both results are not inconsistent if one takes into account that the presence of oxide is only one of the necessary requirements to appear luminescence. The second necessary requirement consists in the presence of nanoclusters provided the quantum confinement effect inside pores. It becomes obvious, that in case of electric spark discharge treatment, the nanoclusters of Ge and oxide will form more strong structure, than in case of anodization [2].

The similar explanation is also confirmed by the results of paper [3], where the anodized layers of porous germanium were oxidized at 600°C in oxy-

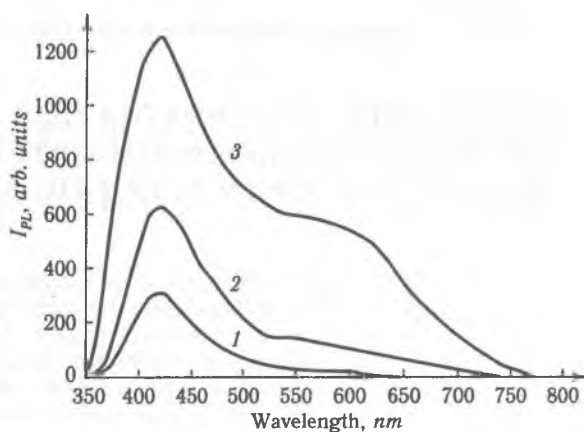


Fig. 3. Photoluminescence spectra of porous germanium: 1 — with oxide layer formed as the result of electric spark treatment; 2 — after mechanical removal of thin oxide layer; 3 — after more complete removal of oxide layer

gen and nitrogen atmosphere in the ratio 1 : 9, respectively. The results of this work show the strong shift of photoluminescence maximum to the short-wave direction. This phenomenon is accompanied by approximately 150-fold increase in photoluminescence efficiency comparing to the initial value. This effect is explained [3] as displacement of bound hydrogen and as its substitution by oxygen. Thus, the part of oxide increase that allows to make conclusion about the decisive role of localized states on $\text{Ge}-\text{GeO}_2$ interface in shaping of photoluminescence.

From results of [2] one can see, that in samples obtained by stain-etching, there is photoluminescence peak with maximum near 420 nm (with wavelength of exciting light 325 nm), whereas, for the anodized samples, the peak lies within the range $560 \dots 580 \text{ nm}$ (but at excitation by wavelength 488 nm). The necessity to use excitation at the greater wavelength in the second case is explained, obviously, by abrupt degradation of photoluminescence. It prevents the possibility to compare the results even within the paper. At the same time, in our case, when electric spark discharge is used to obtain porous germanium, both maxima (420 nm and 540 nm) are present in photoluminescence spectrum under excitation with wavelength 337 nm (fig. 4). Taking into account that in [2] excitation energy for photoluminescence of anodized porous germanium is lower than in present work, it is possible to assert, that the corresponding maxima are identical with the high probability.

The fact [2] that photoluminescence of chemically etched layers of porous germanium degrades promptly and strongly enough under the influence of laser excitation while the noticeable decrease of photoluminescence is not observed for our samples under the same conditions, should be taken into

account. This proof out of the photostimulated changes we explain by the assumption that nano-

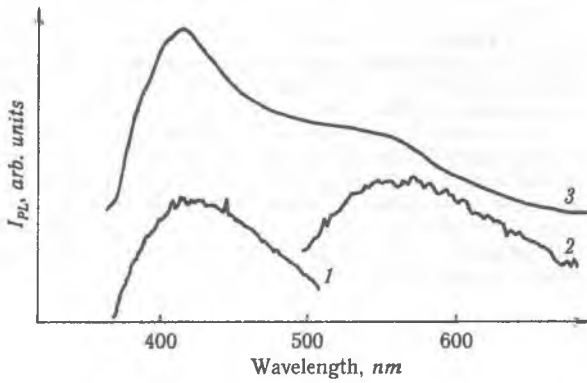


Fig. 4. Photoluminescence spectra of porous germanium: 1 — obtained by stain etching ($\lambda_{exc} = 325 \text{ nm}$); 2 — obtained by anodization ($\lambda_{exc} = 488 \text{ nm}$); 3 — obtained by spark discharge ($\lambda_{exc} = 337 \text{ nm}$)

clusters of germanium (1) in our structure are implanted in solid bed of oxide (2) (fig. 5).

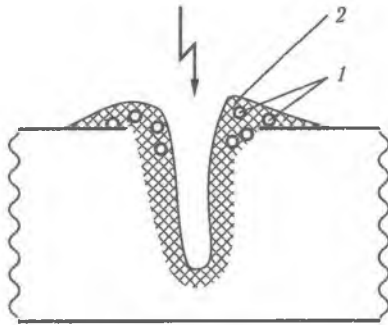


Fig. 5. Schematic image for dislocation of Ge clusters in oxide layer after electric spark discharge treatment: 1 — Ge clusters; 2 — oxide layers

In the paper [7] devoted to studies of Ge clusters in porous silicon, the diminution in photoluminescence intensity and shift in its maximum to the short-wave direction after one year of storage was demonstrated. This result is stipulated by oxidation through Ge clusters, i. e. increase in width of oxide layer and diminution in germanium core of cluster. The similar phenomenon also takes place with Si clusters in porous silicon during long-time storage on air and at annealing with saturated carbon (carbonic treatment) [14]. The absence of the noticeable result for the given effect in our samples and also the absence of luminescence degradation under excitation by UV laser testifies to the initial prevention in them from the further oxidation of nanoclusters through oxide film. This «defence» may be explained by the steeping of nanoclusters in rather thick oxide layer that is stipulated by procedure of sample preparation.

The research of the influence for the small doses of γ -irradiation has shown that it led to decrease in photoluminescence efficiency with simultaneous

smoothing and broadening of spectrum (fig. 6). The obtained effect can be explained by formation of

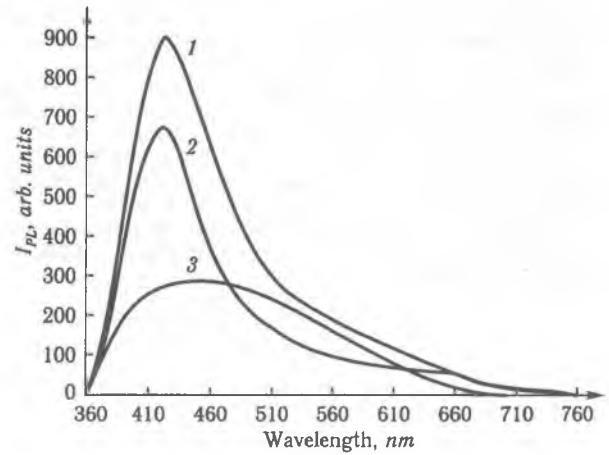


Fig. 6. Photoluminescence spectra of porous germanium: 1 — initial spectrum; 2 — after storage on air during one month; 3 — after γ -irradiation with dose $5 \cdot 10^4 \text{ rad}$.

additional centers for light absorption. These centers allow to recombine radiatively for donor—acceptor pairs with low energy.

3. Conclusion

1. The decisive role of Ge—GeO₂ interface during photoluminescence of porous germanium is shown.

2. The absence of noticeable degradation in intensity of photoluminescence of porous germanium during long-time storage is explained by preliminary good prevention of Ge clusters during material production by using the electrical spark discharge method.

3. The decrease in photoluminescence intensity of porous Ge with simultaneous smoothing and broadening of spectrum under influence of small γ -irradiation doses is explained by formation of additional centers for light absorption in oxide layer.

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