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Silicon doped with sulfur as a detector material for high speed infrared image converters

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Abstract.

The work aims at approaching the solution of the problem of developing sensitive silicon detectors for high speed IR imaging devices which are semiconductor – gas discharge systems. Among the requirements to detectors is their operation at the temperature which is somewhat higher than that of liquid nitrogen. To meet this requirement, a set of deep impurities is analyzed. It is emphasized that silicon doped with sulphur is a good choice to reach the aim. The doping of silicon with sulphur is done by the technique of high temperature diffusion. Data of the Hall measurements indicate the presence of large density of shallow donor levels in the material obtained. To compensate them, acceptors are introduced afterwards with using radiation doping techniques. Testing of the fabricated detectors in the converter setup shows that they provide imaging of IR fields of temperature $T \sim 270\ ^0C$ with the temporal resolution in the order of 3 μs.

Introduction.

Study of high speed processes by optical instruments becomes an important issue of modern research and technology. Nowadays, the most advanced are high speed photography methods that are based on applying vacuum tubes and silicon CCD devices. These techniques cover the visible and near IR spectral range, up to the wavelength $\lambda \sim 1.1\ \mu m$. However, a number of applications require the availability of methods that could provide high speed imaging at longer wavelengths of IR, with the recording rate higher than 10^3 *frames/s*. An important non-solved problem is the spatially resolved high speed thermography of objects heated up to relatively low temperatures, which are in the order of $200 - 300\ ^0C$.

The high speed conversion of IR images into visible can be done with semiconductor – gas discharge imaging devices. It has been demonstrated that the devices can perform the high speed visualization of IR laser fields in the spectral range $1 - 10.6\ \mu m$ - see, e.g., [1-3]. We notice that optical fields emitted by lasers are, in general, of a high power. Therefore, in general, detectors of a relatively low sensitivity can be used for purposes of diagnostics of IR laser fields. Contrary, to solve the problem of the high speed thermography, one needs to develop rather sensitive semiconductor detectors for converters as compared to those applied in laser diagnostics devices. The present paper deals with results of the research aimed, finally, to develop such sensitive planar detectors. In addition to the high sensitivity in the IR range of spectrum, the main specific demands to the detector material are: *i*) to ensure the high informative capacity of converted images, the active aperture of the detector wafer should be ~ 30 mm in diameter, which requires the corresponding spatial homogeneity of the detector characteristics; *ii*) stability of operation when being in contact to the gas discharge plasma.

The analysis of the problem shows that the needed sensitivity of systems that are designed for purposes of high speed thermography, can be provided by the application of silicon doped with sulfur. It is known that sulfur produces in silicon a set of donor levels of different energy [4,5]. It is essential that, among these levels, there is the center E_c-0.18 eV that fits well for the purpose of thermography in the considered temperature range. The material can provide the needed characteristics of the imaging system at the detector temperature of the order of that for liquid nitrogen. This is an advantage of sulfur as compared to other deep impurities, such as zinc, indium, or selenium. In the present work, the doping of silicon with sulfur is performed by high temperature diffusion of the element into the monocrystalline silicon wafers. To evaluate the efficiency of the converter at applying the developed detectors, the corresponding measurements are made. It is demonstrated that using *Si(S)* provides imaging of thermal fields at the temperature 250 – 300 ^0C at the exposure time on the microsecond scale.

Analysis of performance of Si detectors doped with various deep impurities

Silicon doped with deep impurities has been applied in infrared technology for a long time – see, e.g. [6]. Among deep impurities, the most studied are gold, platinum, indium, zinc, selenium, sulfur, and some others. Before making analysis of applicability of different deep impurities for the purpose of high speed thermography, we point out that one of practical requirements to the corresponding device is that the operation conditions of a detector can be provided by using liquid nitrogen as a cooling agent.

For the comparative study four materials are chosen which are *Si:Zn*, *Si:S*, *Si:Se* and *Si:In*. It has been evaluated the temperature dependence of response of the detectors for real parameters of detector materials listed in Table. An approach similar to that realized in the work [7] for *Si:In* detectors has been applied. Data for Si:In are borrowed from the paper [7], and for other impurities are taken from the review article [6]. As a first step in the analysis, temperature dependences of main properties of detectors as functions of temperature have been defined. To do this, the charge neutrality equation for free carriers and impurity centers is numerically solved. To characterize a photodetector performance, a relative photoconductivity is calculated for some typical conditions close to a real application.

Table. Main parameters of detectors used in calculations

Semi-conductor material	Impurity ionization energy, [eV]	Impurity density, [cm^{-3}]	Photoionization cross section, [cm^2]	Capture rate, [cm^{3}s^{-1}]	Density of compensating shallow impurity, [cm^{-3}]
Si:In	0.16 0.11	1.0×10^{17} 2.0×10^{14}	3.3×10^{-17} 3.3×10^{-17}	2.0×10^{-7} 2.0×10^{-7}	1.0×10^{14}
Si:S	0.38 0.177	5.0×10^{15} 5.0×10^{15}	1.1×10^{-16} 1.1×10^{-16}	8.4×10^{-8} 8.4×10^{-8}	1.5×10^{14}
Si:Se	0.305 0.205	5.0×10^{15} 5.0×10^{14}	5.8×10^{-17} 5.8×10^{-17}	2.2×10^{-8} 2.2×10^{-8}	1.5×10^{14}
Si:Zn	0.31	2.0×10^{16}	2.0×10^{-16}	3.0×10^{-7}	1.0×10^{14}

Next parameters of the experimental setup are used in calculations:

i) a detector is irradiated from a blackbody source which emissive area is 1 cm^2. The image of the source of $T = 250$ ℃ is built on a detector surface with the mirror optical system of the 25 *cm* focal length and of the aperture of f/5.0. It is assumed that the image is projected onto the detector area with the 1:1 magnification.

ii) electric field in the detector volume is 5.0×10^3 *V/cm*. The so called "dark" current of a detector (that is, the current at the absence of irradiation from a heated object) is determined by the thermally activated semiconductor conductivity and, additionally, by the 20 ℃ background radiation incident on the photodetector from the environment. The field of view angle for this background radiation is assumed to be 30°.

We define the relative photoconductivity R_{phc} as the ratio of the difference between photocurrent the blackbody image J_{BB} and the dark current J_{DC} to the dark current:

$$R_{phc} = \left(J_{BB} - J_{DC}\right) / J_{DC}$$

Fig. 1 shows calculated dependences of response to the 250°C blackbody radiation as dependent on the detector temperature. Data are obtained for detectors doped with different impurities. One can see that a rather high response is demonstrated by *Si:Zn* and *Si:Se* detectors. In general, the temperature at which the response starts to drop decreases at decreasing the energy of impuruty ionization. For parameters used in calculations, the lowest sensitivity is observed for *Si:In* detectors.

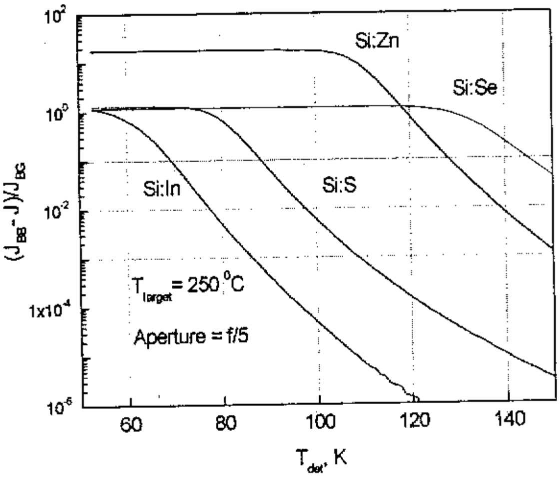

Fig. 1. Theoretical relative response of different detectors for some typical conditions of doping as shown in Tabl.

When using liquid nitrogen as a cooling agent, one can cool the image converter cell down to the temperature T_{det} = 80 – 85 *K*. According to the data shown in Fig. 1, one can expect in experiments the highest relative response to the IR radiation for *Si:Zn* and *Si:Se* detectors, whereas the *Si:In* material is able to show the response only of the order of 5×10^{-3}. The last result means, particularly, that *Si:In* is not a proper material for thermography applications: Because of low sensitivity it is difficult to extract the useful information from the overall signal that contains noise. As follows from the data obtained, detector materials that potentially may satisfy the requirement of high sensitivity at the considered conditions, are *Si:Zn, Si:Se* and *Si:S*.

We have to point out, however, that the above analysis evaluates only the steady state response of detectors. As concerns the high speed application of the semiconductor – gas discharge IR image converters, one has to consider the ability of these devices to respond to *fast temporal* variations of incoming IR fields. Experimental and theoretical investigations of the dynamic operation of the devices reveal their expressed nonlinear behavior in transient modes – see [8,9]. In general, the speed of response is defined by two main processes: these are the rate of potential relaxation in the semiconductor – gas discharge gap cell, and the rate of variation of charge carriers density in the discharge gap [8]. In particularly, it has been established that the ability of the high speed performance is essentially dependent on the density of electric current that flows in the converter before detector is excited with a pulsed radiation. Experiments and the theoretical analysis of the problem gives the evidence that, to achieve the speed of operation of the order of 1 *µs*, the density of "dark" current in the device should be higher than ~ 1 mA/cm^2.

Therefore, to consider the applicability of different detector materials for the high speed IR imaging, it is appropriate to determine the dark current density of detectors at typical conditions of operation. The corresponding temperature dependences for the parameters of materials that are listed in Table, are plotted in Fig. 2. Calculations are performed for the electric field strength E = 5×10^3 *V/cm* in a detector volume. Current density of detectors is determined by free carriers that are generated by thermal processes and by the background radiation. It is taken into account that the mobility of free carriers is temperature dependent.

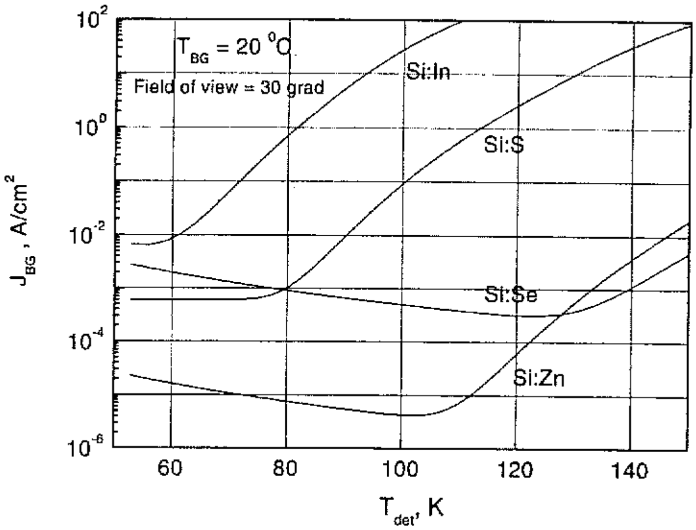

Fig. 2. Calculated dependences of density of "dark" current for detectors at some typical conditions of doping which are given by Tabl.

The analysis of data represented by Figs. 1,2 shows that the operation of the high speed imaging device working at a detector temperature T_{det} = 80 – 85 K is favorable at applying *Si:S* detectors. This material can provide the sensitivity to IR radiation emitted by bodies of the temperature $T \sim 250\ ^{0}C$ (Fig. 1). At the same time, as follows from Fig. 2, the "dark" current density of the device is rather large which fits to the requirement of the high speed operation. We notice also that *Si:S* detectors demonstarte their ability to work stable while contacting the gas discharge plasma in the considered converters [10]. Therefore, in the present research, *Si:S* has been chosen as a detector material.

Technique of doping silicon with sulfur and results obtained.

The sulfur impurity was introduced into wafers via the high temperature diffusion process. Different types of *p*-silicon grown by Czochralski method have been used as a starting material for introducing the impurity. Two methods of doping have been applied. One of them is based on processing of silicon wafers at the presence of sulfur vapor in closed silica tubes. The typical pressure of sulfur vapor at the diffusion temperature ($T \sim 1200\ ^{0}C$) is in the order of 1 atmosphere. This technology is similar to the method that was earlier applied, e.g. in the work [11]. The other technological routine does not require the using of closed silica tubes. It includes two main stages of the process. There, at first, the subsurface layer of a wafer is doped with sulfur in an open air from an organic substance that is deposited onto the surface. The second phase of the process takes a long period of time, in the course of which the diffusion of sulfur into the crystal volume occurs. The last method is similar to that described earlier [12].

It has been found that all doped samples reveal, in addition to deep levels, the presence of a relatively high density of shallow donor levels with the energies E_c-0.11 eV and E_c-0.08 eV (as it can be evaluated with the Hall technique – see an example of the corresponding Hall data in Fig. 3). Evidently, the presence of shallow centers is the unwanted property of the detector material. Even at the temperature of liquid nitrogen, they give rise to a much higher "dark" current density of detectors as compared to the corresponding theoretical curve in Fig. 2 which results in the crucial drop of sensitivity of the imaging device.

According to literature data, the deep levels spectra of *Si:S* may be rather sensitive to the mode of cooling of samples after their high temperature processing. Usually, doped crystals are quenched, see, e.g., [11]. It is done by dropping of hot samples into water or oil. Such a procedure is not applicable in our case because of large dimensions of detectors: Typically, a fabricated detector has the diameter of 35 *mm* and the thickness of 1 *mm*.

In order to reduce the negative role of shallow levels in the operation of detectors, after doping with sulfur, samples have been processed by irradiation either with γ- rays or with electrons of high energy. Such procedures are known to introduce the acceptor centers (*A*-centers) that compensate the donor impurity, see, e. g. [13]. While applying this technique, it was possible to reduce substantially the density of uncompensated shallow donor levels, and, in this way, to shift the behavior of *Si:S* detectors close to the "good" theoretical one which is represented by corresponding curves in Figs. 1,2. A result of such processing of one of the samples is shown in Fig.3.

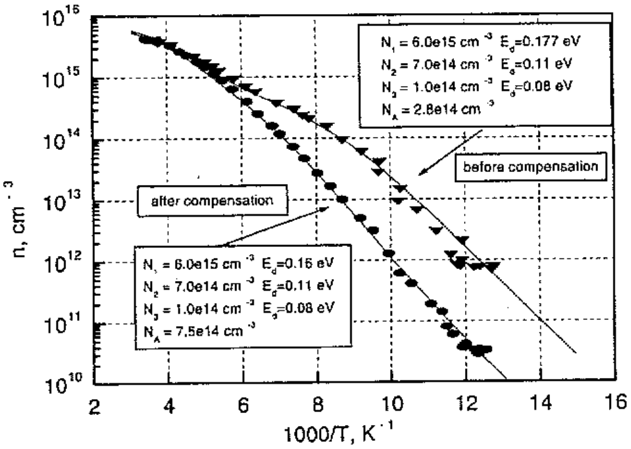

Fig. 3. An example of the Hall data for a *Si:S* sample before (upper points) and after (lower points) compensation with γ- rays. Points are experimental data. Continuous lines show the results of theoretical fitting to experimental points. N_1, N_2, N_3 – densities of levels introduced due to diffusion of sulfur. N_A – density of compensating acceptors.

The operation of fabricated detectors was tested with using a laboratory version of the semiconductor – discharge gap image converter – see the details of such experiments, for example, in our previous papers [3,9]. In the present experiments, the gas discharge gap of the thickness d_g = 100 μm was filled with Ar at the pressure $P \sim 0.1$ *atm*. The converter setup was fed with rectangular pulses of voltage which typical amplitude was 0.8 – 0.9 *kV* and pulse duration inside the range 2 – 10 μs. Pulse images formed by glow of the discharge gap were captured by the Sensicam QE camera produced by the PCO company (Germany). The camera exposure time can be controlled in the range $0.5\times10^{-6} - 1000$ *s*.

Preliminary data give the evidence that, when applying the Czochralski grown silicon as a starting material, the radiation methods of compensation can give rather non-homogeneous distribution of the so called "dark" resistivity of detectors at working temperatures. An example of the corresponding "dark" image produced by the converter, is shown in Fig. 4. To our mind, the appearance of non-homogeneities in the detector resistance may be related to non-homogeneous distribution of oxygen in starting silicon crystals. This and similar data could be informative for visualization of effects of radiation doping of silicon. However, the non-homogeneities in detectors reduce the quality of imaging with the device. While applying material that does not manifest such a pronounced formation of defects as shown in Fig.4, we have been able to record the thermal field of temperature $T = 270\ ^0C$ at the exposure time of 3 μs (Fig. 5).

Fig. 4. An example of the spatial distribution of "dark" glow in the device. The shown area is 22 *mm* in diameter.

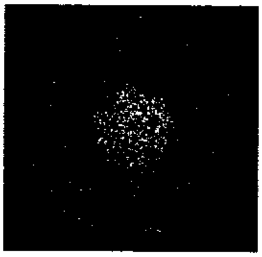

Fig. 5. A result of recording of a thermal field of temperature $T = 270\ ^0C$ at the exposure time 3 μs (in the center of the picture). The image is obtained by subtraction of the background signal from the picture captured at the excitation of detector by the radiation from the heated object.

Conclusion

The present work demonstrates that silicon doped with sulfur can be used in semiconductor – gas discharge image converters designed for high speed thermography. The fabricated detectors provide recording of a thermal field of temperature $T \sim 270\ ^0C$ at the exposure time of ~ 3 μs. In the further research, we hope to increase the sensitivity of detectors, and the speed performance of image converters equipped with these detectors.

Acknowledgments

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