Investigation of the transient characteristics of S-diodes based on silicon compensated by vanadium

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Abstract. To obtain more photosensitive S-diodes, silicon should be compensated for by impurities, which increase the photosensitivity of the original crystals. Diffusion of vanadium in silicon was carried out in evacuated or open quartz ampoules at a temperature of 900-1250 °C for 2-20 hours. Silicon wafers 0.5-1.0 mm thick and an alloying element of vanadium were placed in the ampoule. Usually used n-Si with ρ ~ 5 ÷ 200 Ω·sm and with a thickness of 0.2-0.5 mm. The concentration of deep levels introduced during diffusion was 10¹⁴ cm⁻³. The resistivity of silicon after diffusion increased to 10³-10⁴ Ω·sm at 300 K, and the diffusion length Ld decreased to 10-30 μm. S-diodes were made in a vacuum by melting aluminum and Au + 0.1% Sb alloy at 700 °C for 1 min. The contact area (S) is approximately 0.2 mm², the base thickness d = 0.2-1.0 mm. Attitude d / Ld = 10 ÷ 100. I_incline / I_inclusion in a wide range of currents is linear, where I_incline / I_inclusion the charge is Q_cr = 3.52·10⁻⁹ C. In this case, the average concentration of injected current carriers in the base is n = 5.44·10¹³ cm⁻³, which is in good agreement with the concentration of electroactive atoms V in Si, determined by capacitive methods. The dependence 1 / V_i - 1 / V_o for S-diodes from n-Si <V> has a complex form at each temperature and is approximated by two exponents. The obtained experimental results, their analysis and conclusions on S-diodes from Si <V> can be used as a temperature relay, photo relay, switches and photodetectors controlled by the sensitivity current.

1. Introduction
Currently, the development and production of semiconductor devices and integrated circuits with a large number of elements per unit volume of material require a significant improvement in the perfection of the structure of silicon - the main material of semiconductor micro- and optoelectronics. These requirements are primarily due to the fact that in the process of manufacturing and subsequent operation, semiconductor materials and devices based on them are exposed to temperature and other external factors, as a result of which a number of structural impurity defects are formed. Doping of semiconductor materials with unconventional impurities, such as transition and rare earth elements, is one of the main methods for the controlled introduction of a certain type of defects and
allows one to control the properties of semiconductor materials and devices based on them within the micron range.

Studies of the properties of silicon doped with elements of the transition group of the periodic table showed that these elements create deep levels in the band gap of silicon, significantly affecting the photoelectric properties of silicon, especially device structures based on it. However, the properties of silicon doped with vanadium are relatively poorly studied. The photoelectric and capacitive properties of silicon doped with vanadium are practically insufficiently studied, and there are no data in the literature on the device structures of silicon doped with vanadium.

S-diode devices, which have a section of negative differential resistance (NDR) in the forward direction of the I-V characteristic, are made of a compensated material with a high specific resistance. For the first time, negative resistance (NR) was observed at 77 K in germanium diodes doped with iron and gold. Then S-diodes were made of Si and GaAs with various impurities [3,4,5,6,7]. A review of experimental and theoretical studies on the study of S-diodes is given in [8,10]. The theoretical mechanism of the NR (τ - mechanism) was proposed in the theoretical analysis given in [1].

The main parameters of S-diodes are the “breakdown” voltage $V_{br}$, the minimum voltage after “breakdown” $V_{min}$, the “breakdown” current $I_{br}$, and the recovery time $\theta$ after the diode is turned off. As numerous studies have shown, S-diodes have much greater functionality than other semiconductor devices. They can be used as: a key, an optoelectronic phototrigger switch, a trigger, a generator of relaxation and harmonic oscillations, a noise generator of a uniquely high power resonant and parametric amplifier, a narrow-band filter, a highly sensitive light indicator, including infrared, threshold light source, spectral composition converter light, highly sensitive sensor of magnetic field, pressure, temperature, threshold memory element, logic elements, etc.

The theories of NDR in S-diodes can be reduced to several main mechanisms: 1) An increase in the lifetime with the level of injection of at least one type of current carriers. In the case of the diffusion approximation, the change should be relatively large-2-3 times. In the drift approximation, the change in $\tau$ is rather small. 2) An increase in the injection coefficient of the pn junction with increasing current. 3) Impurity breakdown in combination with injection from p-n - junction [1]. 4) Joule warming up. 5) Increase in the mobility of current carriers. 6) Change in bipolar mobility [9].

To obtain S-diodes, the following conditions must be met:

1. The length of the diffusion displacement of current carriers at low injection should be less than the base thickness ($L_D << d$).
2. Base resistance should be high.
3. Modulation, the base resistance should grow superlinearly with the injection level due to the growth or injection coefficient of the transition.

The first two conditions provide a large voltage drop in the forward direction at a low injection level, the third condition is necessary for the formation of an NDR section with an increase in the injection level. Illumination of the base of the S-diode with light leads to a decrease in its resistance and due to the positive feedback of the photo, the sensitivity of the S-diodes turns out to be higher than that of the base material with ohmic contacts. When illuminated, the S-diode current increases and $V_{op}$ decreases.

To obtain more photosensitive S-diodes, silicon should be compensated for by impurities, which increase the photosensitivity of the original crystals. As studies have shown, the photoconductivity (PhC) of silicon doped with vanadium makes it possible to create S-diodes.

2. Method

Manufacturing technology of S-diodes To obtain an S-diode suitable for manufacturing, compensation of the initial crystals with deep level (DL) impurities is usually used [10]. Such impurities are effective centers of compensation and, under certain conditions, increase the resistivity due to the trapping of mobile carriers at the DL.

Diffusion of vanadium in silicon was carried out in evacuated or open quartz ampoules at a temperature of 900-1250 °C for 2-20 hours. Silicon wafers 0.5-1.0 mm thick and an alloying element of vanadium were placed in the ampoule. In the case when diffusion was carried out in open
ampoules, alloying elements were deposited on both sides of the silicon wafer surface. The resistivity $\rho$ and the type of conductivity of the original silicon were selected depending on the required parameters of the diodes. Usually used n-Si with $\rho \approx 5 \div 200 \, \Omega \cdot \text{cm}$ and with a thickness of 0.2-0.5 mm. The concentration of deep levels introduced during diffusion was $10^{14} \, \text{cm}^{-3}$. The resistivity of silicon after diffusion increased to $10^{3} \div 10^{4} \, \Omega \cdot \text{cm}$ at 300 K, and the diffusion length $L_d$ decreased to 10-30 μm. After controlling the type of conductivity and resistivity, careful etching was carried out in a mixture of HF + HNO3 (1:3) and the samples were washed. Then they were cut into rectangles with a size of $1.5 \times 1.5 \times (0.3-10) \, \text{mm}^3$.

S-diodes were made in a vacuum by melting aluminum and Au + 0.1% Sb alloy at 700 °C for 1 min. The contact area (S) is approximately 0.2 mm², the base thickness $d = 0.2-1.0$ mm. The ratio $d/L_d \approx 10 \div 100$.

2.1. Experimental apparatus

The study of transient characteristics (TCh) is of interest both from the point of view of studying the physical processes occurring in diodes, and from the point of view of their practical application. Investigation of the HRC of S-diodes was carried out using generators of shifted rectangular paired pulses with an adjustable delay [3]. The measurement scheme is shown in Fig. 1. Generators of the G5-7A, G5-15, G5-54 types were used as a source of pulses. The voltage and current waveforms were observed using an S8-13 oscilloscope.

![Figure 1. Scheme for measuring transient characteristics](image1.png)

**Figure 1.** Scheme for measuring transient characteristics

![Figure 2. The shape of the voltage pulse on the S-diode (a) and the current through S-diode (b)](image2.png)

**Figure 2.** The shape of the voltage pulse on the S-diode (a) and the current through S-diode (b)

In the voltage generator mode, the “breakdown” current was investigated in the pulsed mode (the current through the diode was limited only by the internal resistance of the generator and a low resistance for measuring the current). In fig.2 (a) shows the shape of the voltage pulse in the S-diode.
At the very beginning of the pulse, a section of rapid voltage growth is observed, then the growth slows down and \( V \) tends to a stationary value. The shape of the current pulse through the S-diode is shown in Fig. 2 (b). When the current in the pulse increases to a certain critical value, a breakdown occurs. The time from the beginning of the pulse to the beginning of the breakdown (turn-on time) decreases with increasing current. \( t_{on} \) is determined by some charge \( Q_{cri} \), which must enter the base of the diode before the start of the breakdown. The current flowing through the diode is determined by the sum of the through current \( J_0 \) and the current providing the accumulation of charge \( Q \):

\[
I = I_0 + \frac{Q}{t}
\]

Knowing the values of \( Q_{cri} \), one can estimate the concentration of current carriers, assuming that these carriers are uniformly distributed under the p-n - junction. Then

\[
n_0 = \frac{Q_{cri}}{qs} \]

where \( q \) is the electron charge; \( S \)-area of p-n-junction; \( d \)-base thickness.

### 2.2. Problem formulation

The goal of this work is to establish the possibility of creating photosensitive S-diodes based on silicon compensated by vanadium, which ensure efficient operation at 300 K.

### 3. Results and Discussion

Figure 3 shows the dependence of the current in a pulse on the inverse turn-on time of the S-diode from n-Si \(<V>\) at \( T = 300 \) K. As can be seen from the figure, \( I_{incline} \sim 1/t_{inclusion} \) in a wide range of currents is linear, where \( I_{incline} > I_{rec} \). Determined by the slope \( I_{incline} \sim 1/t_{inclusion} \), the charge is \( Q_{cri} = 3.52 \times 10^{-9} \) K. In this case, the average concentration of injected current carriers in the base is \( n = 5.44 \times 10^{13} \) cm\(^3\), which is in good agreement with the concentration of electroactive atoms V in Si, determined by capacitive methods [2].

![Figure 3](image)

**Figure 3.** Dependence of the current in a pulse on the reverse turn-on time of the S-diode from n-Si \(<V>\) at \( T = 300 \) K.

The speed of the S-diodes is limited by the recovery time of the breakdown voltage \( \theta \), which is determined using paired pulses. In the mode of the current generator, the voltage across the test sample will be proportional to the base resistance \( n \) if the concentration of mobile carriers at

\[
n_t \sim \frac{1}{V_x}
\]

\( n_t \) - concentration of mobile current carriers, depending on time
If the dependence has the form
\[ n_i = n(0) \exp\left(-\frac{t}{\theta}\right) \]
then
\[ \theta = -\frac{\Delta t}{\Delta \ln \left(\frac{1}{V_i} - \frac{1}{V_\infty}\right)} \]

where \( \Delta t \) - is the delay time of the second pulse.

**Figure 4.** Schematic representation of oscillograms of voltage pulses taken from the test sample

**Figure 5.** Dependence of the slow component of the recovery time constant of the switching voltage of the second pulse to temperature

Figure 4 shows a schematic representation of oscillograms of voltage pulses taken from the sample under study.
Dependence $\frac{1}{V_t} - \frac{1}{V_\infty}$ for S-diodes from n-Si $<V>$ has a complex form at each temperature and is approximated by two exponentials. Figure 5 shows the dependence of the slow component of the recovery time constant of the switching voltage of the second pulse to the temperature of S-diodes based on Si $<V>$.

The obtained experimental results, their analysis and conclusions on the electrical and photoelectric properties of silicon, compensated by vanadium, can be used for: The created S-diodes can be used as a temperature relay, photo relay, switches and photodetectors controlled by the sensitivity current.

**Table 1. Basic parameters of S - silicon-based diodes with various impurities.**

| Impurity | Conductivity type | Breakdown voltage $V_{\text{br}}$ | Voltage after $V_{\text{br}}$ | $V_{\text{br}}/V_{\text{min}}$ ratio | Breakdown current $I_{\text{br}}$, mA | Exponent $n$ in $I = I_0 \times \Theta^n$ | Sensitivity $K$, μA/lm | Existence temperature range, K |
|----------|-------------------|-------------------------------|-----------------------------|--------------------------------------|------------------------------------|-------------------------------|-------------------------|-------------------------|
| H$\alpha$ | n                 | 12±30                         | 4±8                         | 3±7                                  | 0.4±3                              | 0.35±0.4                      | 1.2±10$^4$             | 100±300                 |
| V        | n                 | 3.8±13                        | 1.8±3.3                     | 1.5±3                                | 0.24±2                             | 0.7                           | 3.0±10$^6$             | 77±300                  |
| Cd       | n                 | 5±15                          | 2±5                         | 4±15                                 | 0.3±1                              | 0.3±0.4                      | 1.6±10$^3$             | 77±300                  |

4. Conclusions
1. The main parameters of the S-diodes were as follows; $V_{\text{br}} = 3.8 \pm 13$ V, $V_{\text{min}} = 1.8 \pm 3.3$ V, $V_{\text{br}}/V_{\text{min}}$ ratio $= 1.5 \pm 3$, “breakdown” current $I_{\text{br}} = 0.24 \pm 2$ mA.
2. It is shown that in S-diodes obtained on the basis of silicon compensated by vanadium, the negative differential resistance is due to the formation (n$^-$-i-n-i-p$^+$) of an uneven distribution of vanadium atoms in the bulk of the material.
3. The transient characteristics of S-diodes based on n-Si $<V>$ are investigated. The speed of the S-diodes is limited by the recovery time of the "breakdown" voltage $\Theta$, which varies from 0.5 to 7 μs.

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