
INFLUENCE OF LIGHT ON WATER DECOMPOSITION AT Al- AND Ti-DOPED SILICON ELECTRODES

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Al ($E = 75$ keV, $D = 1.15 \times 10^{16}$ cm $^{-2}$) and Ti ($E = 125$ keV, $D = 7.6 \times 10^{15}$ cm $^{-2}$) ions were implanted into thermally oxidized n -Si specimens ($\rho = 4 \Omega \times \text{cm}$). The specimens obtained were used as electrodes to study the decomposition of distilled water with Pt or Yb serving as counterelectrodes. The influence of illumination of Si(Al) and Si(Ti) electrodes on the current generation accompanied by water decomposition in the absence of an external electric voltage ($V = 0$) between the silicon electrode and the counterelectrode and in the case where an external positive voltage ($V = +9.7$ V) is applied to silicon electrodes has been studied for the first time. A conclusion has been made that the role of illumination in enhancing the rate of water decomposition is reduced to the enrichment of the near-surface region of the silicon electrode by electrons.

1. Introduction

In our previous works [1–3], we revealed the phenomenon of current emergence in an electrochemical system consisting of two different electrodes immersed into distilled water; the current appeared owing to the reaction of water decomposition $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$. Water is decomposed owing to catalytic properties of electrodes (at least, of one of them) and different electrochemical potentials of electrodes (different work functions needed for electrons to quit them). The current between electrodes (sometimes, the current increases in time) is maintained owing to the electrochemical reactions of H^+ and OH^- ions at the corresponding electrodes (the cathode and the anode, respectively).

In works [1–3], we used various metals, silicon with various physical and chemical states of its surface, and

silicides of metals as electrodes. While carrying out experiments, neither in the absence of an additional external voltage between electrodes ($V = 0$) or when the voltage $V = +9.7$ V was applied, the influence of the natural or artificial illumination on the current was not observed. That is, this means that the process of water decomposition was not caused by photoelectrochemical processes. Nevertheless, if at least one of the electrodes is a semiconductor (in our case, it is silicon), one should expect that, under definite conditions, the current generation (the rate of water decomposition) would depend on the light exposure level, to which the semiconducting electrode is subjected.

In this work, we fulfilled experiments which prove a possibility for the external illumination to substantially affect the current generation process with water decomposition, i.e. they testify that there is an opportunity to transform light energy into electrochemical one.

2. Experimental Technique

We used the polished plates of silicon doped with antimony (n -Si, $\rho = 4 \Omega \times \text{cm}$ with an electron concentration of 1×10^{15} cm $^{-3}$). After cutting off 2×1 -cm 2 specimens and oxidizing the latter at a temperature of 1000 °C in dry O $_2$ environment, a layer of SiO $_2$ oxide (1000 ± 10) Å in thickness was formed on their surface. The thickness of the oxide layer was measured by means of an LEF-3M ellipsometer and using the light wavelength $\lambda = 0.63 \mu\text{m}$.

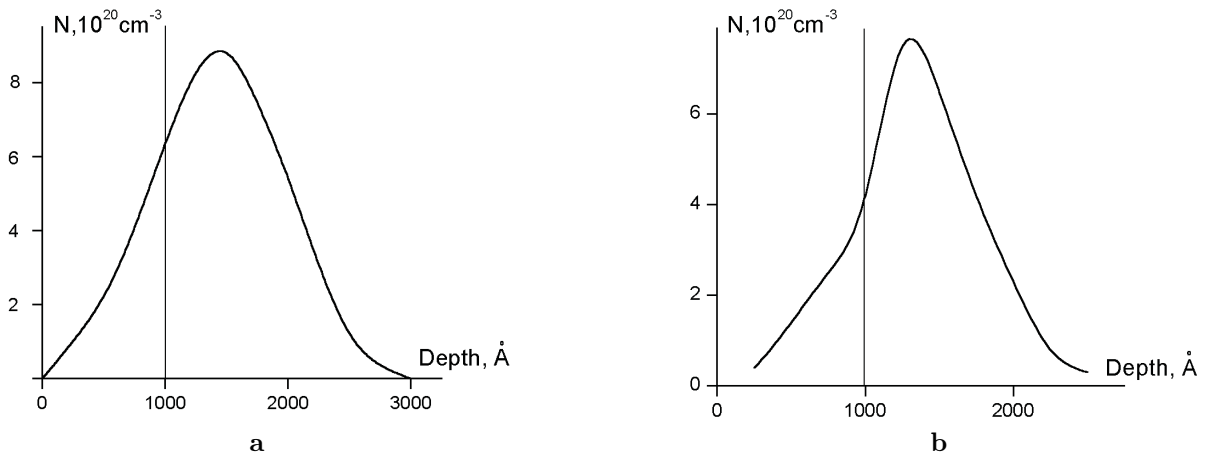


Fig. 1. Distributions of implanted (a) Al ($E_{\text{pulse}} = 75$ keV, $D = 1.15 \times 10^{16}$ cm $^{-2}$) and (b) Ti ($E_{\text{pulse}} = 125$ keV, $D = 7.6 \times 10^{15}$ cm $^{-2}$) ions across the SiO₂(Si) structures. $d_{\text{SiO}_2} = 1000$ Å

One of the oxidized specimens fabricated in such a manner was used for measuring the electron work function and the currents in electrochemical systems SiO₂(Si)–Pt(Yb) by the method proposed by us in works [1–3]. The other SiO₂(Si) specimens were doped with Al or Ti ions. For this purpose, we used a “Vezuvii-1” ionic implanter. The ion energy E and the ion exposure dose D at implantation were as follows: for Al, $E = 75$ keV and $D = 1.15 \times 10^{16}$ cm $^{-2}$; for Ti, $E = 125$ keV and $D = 7.6 \times 10^{15}$ cm $^{-2}$.

In Fig. 1, *a*, the distributions of implanted ion concentrations calculated making use of the TRIM-98 computer program over the depth of the SiO₂(Si) structures are depicted. Down to the depth of 1000 Å, the ions are located in the SiO₂ layer, and – if $d > 1000$ Å – in the near-surface Si one. From Fig. 1, *a* and *b*, one can see that the maximum of the implanted Al concentration is located in silicon at a depth of about 500 Å from the SiO₂–Si interface; while the concentration maximum of implanted Ti lies in silicon at a depth of about 250 Å from the same interface. The curve of Al distribution over the depth of the SiO₂(Si) structure is almost symmetric. At the same time, the curve of Ti distribution near the SiO₂–Si interface demonstrates a faster growth of Ti concentration in comparison with its decay after the distribution maximum. In order to eliminate local structural defects, the SiO₂(Si) structures doped with Al and Ti ions were annealed in vacuum at a temperature of 640 °C for 80 min.

In the course of measurements, first, the work function φ_{el} of electrons for the electrode concerned was determined with respect to the Pt one, the work function of which – $\varphi = 5.32$ eV – is well known. The

technique of measurements was described in works [1, 2] in detail; it includes the measurement of the current magnitudes at applying the voltage ($V = \pm 9.7$ V) to the electrochemical system in both directions. The values of the electron work function at various states of silicon-based electrodes, which were determined using those data, are given in the Table. To calculate φ_{el} , we used the formula that had been derived in our work [1]: $\varphi_{\text{el}} = 5.32$ eV – $qV(I_1 - I_2)/(I_1 + I_2)$, where q is the electron charge, and I_1 and I_2 are the currents in the electric circuit, if the voltage $-V$ or $+V$, respectively, is applied to the Pt electrode.

After the simultaneous immersion of two electrodes into distilled water, we measured the potential difference ΔV between electrodes and the time dependence of the current J between them. In order to compare the efficiency of different electrode pairs with respect to water decomposition and to take into account that the area of electrodes S , the distance L between them, and

Electrode state	Electron work function φ , eV
Thermally oxidized <i>n</i> -Si (SiO ₂)	9.22
Hydrogenation SiO ₂ (H)	13.8
Natural dedydrogenation SiO ₂	9.52
Implanted SiO ₂ (Al)	9.32
Annealing of SiO ₂ (Al) at 640 °C for $t = 80$ min	7.65
Hydrogenation SiO ₂ (Al)	12.3
Etched off SiO ₂ (Al) (state Si(Al))	4.52
After measurements of Si(Al) in 24 h	5.64
Repeated etching Si(Al)	4.63
Implanted SiO ₂ (Ti)	11.8
Annealing SiO ₂ (Ti)	9.67
Etched off SiO ₂ (Ti) (state Si(Ti))	4.22
After measurements of Si(Ti) in 24 h	5.75
Dedydrogenation Si(Ti)	4.68

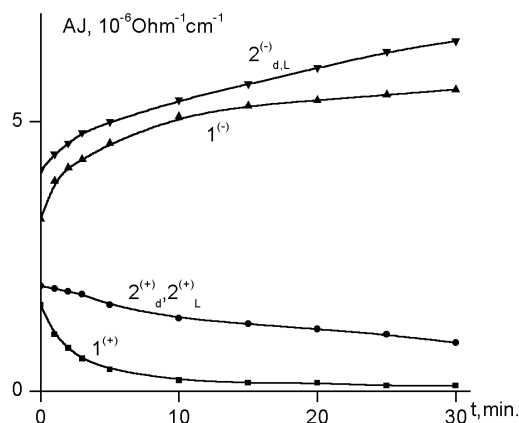


Fig. 2. Time dependences of water conductance $AJ(t)$ for electrode pairs $\text{SiO}_2(\text{Si})\text{-Pt}$ (curves $1^{(+)}$ and $1^{(-)}$) and $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle\text{-Pt}$ (curves $2_d^{(+)}$, $2_L^{(+)}$, and $2_{d,L}^{(-)}$). The subscript d stands for darkness and L for illumination with a 60-W lamp. The signs $(+)$ and $(-)$ correspond to the voltage polarity $V = \pm 9.7$ V on $\text{SiO}_2(\text{Si})$. The AJ -values for curve $2_L^{(+)}$ are larger by about 10% than those for curve $2_d^{(+)}$

the value of the potential difference ΔV were different for different electrode pairs, we built the plots of the dependence of the effective specific conductance of the electrochemical system on time:

$$\sigma_{\text{eff}} = \frac{L}{\Delta V S} J(t) = AJ(t).$$

In the cases where the external voltage $V = \pm 9.7$ V was applied to the electrochemical system, σ_{eff} was calculated by the same formula, but with $\Delta V \pm V$ substituted for ΔV .

3. Experimental Results and Their Discussion

If thermally oxidized silicon $\text{SiO}_2(n\text{-Si})$ is used as one of the electrodes, the corresponding electron work function is governed by the oxide film and the level of filling the latter with H^+ ions (see the Table and work [3]). In the absence of external electric voltage ($V = 0$), owing to the high electric resistance of SiO_2 , very small currents ($J = (5 \times 10^{-9} \div 1 \times 10^{-7} \text{ A/cm}^2)$) are observed in the electrochemical system $\text{SiO}_2(\text{Si})\text{-Pt}$; moreover, they diminish almost to zero rather quickly (within tens of seconds). Therefore, in Fig. 2, we presented the dependences $AJ(t)$ for the systems $\text{SiO}_2(\text{Si})\text{-Pt}$ and $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle\text{-Pt}$ only for the case with a non-zero external voltage ($V = \pm 9.7$ V) across them.

Figure 2 demonstrates that, after Al implantation and annealing of the structures, the values of AJ (curves $2^{(\pm)}$) increase in comparison with those for non-implanted structures (curves $1^{(\pm)}$). Moreover, at $V = +9.7$ V on the $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle$ electrode, a small difference (of the order of 10%) between the AJ -values measured in darkness (curve $2_d^{(+)}$) and under illumination with an incandescent 60-W lamp located at a distance of 25 cm from the $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle$ electrode (curve $2_L^{(+)}$), was observed for the first time. Higher currents at illumination arise owing to the excitation of electrons from the energy levels created by the Al-impurity in SiO_2 and Si. These electronic transitions manifest themselves at a depleting voltage $V = +9.7$ V at the $\text{SiO}_2(n\text{-Si})\langle\text{Al}\rangle$ electrode. In the case of $V = -9.7$ V on the $\text{SiO}_2(n\text{-Si})\langle\text{Al}\rangle$ electrode, the AJ -currents in darkness and under illumination did not differ from each other (curves $2_{d,L}^{(-)}$), because, in this case, the concentration of electrons on the electrode surface is determined by their flux from the bulk into $n\text{-Si}$. Note that the growing-in-time character of curves $2_{d,L}^{(-)}$ and $1^{(-)}$ stems, to a great extent, from the hydrogenation of the $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle$ structure, which gives rise to the increase – in time – of the potential difference between the Pt and $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle$ electrodes.

The dependences $AJ(t)$ changed substantially after the $\text{SiO}_2\langle\text{Al}\rangle$ layer having been etched in a diluted (15%) HF acid (Fig. 3). After such a procedure, we had an $n\text{-Si}\langle\text{Al}\rangle$ structure, in which the near-surface layer about 2000 Å in thickness was an Al-compensated silicon; its electron concentration (the Sb impurity) before implantation was about $1 \times 10^{15} \text{ cm}^{-3}$. After the $\text{SiO}_2\langle\text{Al}\rangle$ layer had been etched, the electron work function for the $\text{Si}\langle\text{Al}\rangle$ electrode decreased drastically, down to 4.52 eV (see the Table); moreover, in the Pt– $\text{Si}\langle\text{Al}\rangle$ system, the Pt electrode became a cathode, whereas earlier, in the Pt– $\text{SiO}_2(\text{Si})\langle\text{Al}\rangle$ system, it was an anode.

The absence of isolating influence of the $\text{SiO}_2\langle\text{Al}\rangle$ film enables a considerable current to manifest itself in the Pt– $\text{Si}\langle\text{Al}\rangle$ system at $V = 0$ owing to a potential difference between the Pt and $\text{Si}\langle\text{Al}\rangle$ electrodes (Fig. 3, curves 1_d and 1_L); in this case, the values of $AJ(t)$ were approximately two times larger if the $\text{Si}\langle\text{Al}\rangle$ electrode were illuminated, in comparison with those under darkness conditions. That is, there is the strong enough effect of the transformation of light energy into electrochemical one (the current generation with the decomposition of water molecules: $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$).

As is evident from Fig. 3, a substantial growth of the $AJ(t)$ -values is observed, if an additional voltage

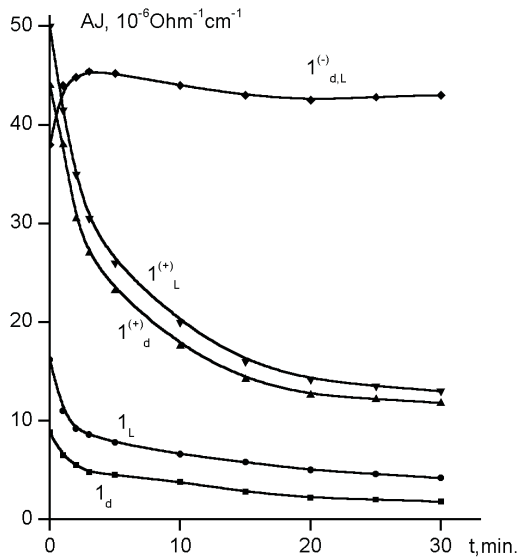


Fig. 3. Time dependences of water conductance for the electrode pair Si<Al>-Pt after etching off the SiO₂<Al> layer from the SiO₂(Si)<Al> electrode. Curves I_d and I_L correspond to $V = 0$, and curves $I_d^{(+)}$, $I_L^{(+)}$, and $I_{d,L}^{(-)}$ to $V = \pm 9.7$ V on the Si<Al> electrode. The subscript d stands for darkness and L for illumination

$V = +9.7$ V is applied to the Si<Al> electrode (curves $I_d^{(+)}$ and $I_L^{(+)}$). This circumstance evidences for the enhanced catalytic decomposition of water at structural inhomogeneities of the Si<Al> surface, due to the presence of strong local electric fields here [1–3]. A reduction of the $AJ(t)$ -values in time for curves I_d , I_L , $I_d^{(+)}$, and $I_L^{(+)}$ was induced by oxidation of the Si<Al> surface, for which the growth of the φ -value was observed (see the Table). After applying the voltage $V = -9.7$ V to the Si<Al> electrode, the growth of its φ is caused by the hydrogenation of the electrode. Note that, although the $AJ(t)$ quantity has considerable magnitudes, it demonstrates relatively small variation in time if the additional voltage $V = -9.7$ V is applied to the Si<Al> electrode. In this case, the illumination of the electrode does not result in the increase of the $AJ(t)$ -values (curves $I_d^{(-)}$ and $I_L^{(-)}$ coincide), because, at $V = -9.7$ V, the electrode becomes electron-enriched owing to this additional external voltage V .

Another metal impurity, which was implanted into SiO₂(Si), was titan. In contrast to aluminum, titan creates substantially deep energy levels in the energy gap of Si: two donor ($E_v + 0.26$ and $E_c - 0.27$ eV) and one acceptor ($E_c - 0.08$ eV) levels [4]. Since the concentration of those levels in the implantation region is higher than the concentration of antimony ($1 \times 10^{15} \text{ cm}^{-3}$) which

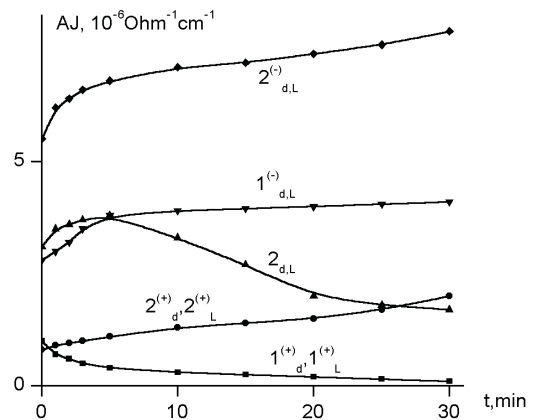


Fig. 4. Time dependences of water conductance for the electrode pairs SiO₂(Si)<Ti>-Pt (curves $I_d^{(+)}$, $I_L^{(+)}$, and $I_{d,L}^{(-)}$) and SiO₂(Si)<Ti>-Yb (curves $2_{d,L}$, $2_d^{(+)}$, $2_L^{(+)}$, and $2_{d,L}^{(-)}$). Curve $2_{d,L}$ corresponds to $V = 0$ and $V = \pm 9.7$ V on the SiO₂(Si)<Ti> electrode. The AJ -values for curves $I_L^{(+)}$ and $2_L^{(+)}$ are larger by about 10% than those for curves $I_d^{(+)}$ and $2_d^{(+)}$, respectively

dopes n -Si, it is these levels that govern the conductance in the implantation region of silicon which turns out electron-depleted.

In Fig. 4, the dependences $AJ(t)$ for SiO₂(Si)<Ti>-Pt (curves $I_d^{(+)}$, $I_L^{(+)}$, and $I_{d,L}^{(-)}$) and SiO₂(Si)<Ti>-Yb (curves $2_{d,L}$, $2_d^{(+)}$, $2_L^{(+)}$, and $2_{d,L}^{(-)}$) electrode pairs after annealing of implanted structures at a temperature of 640 °C for $t = 80$ min are depicted. The illumination of the SiO₂(Si)<Ti> electrode increases the current by approximately 10%, but only if a positive voltage $V = +9.7$ V is applied to this electrode, i.e. the same situation is observed, as when Al ions were implanted into SiO₂(Si) structures.

The growth of AJ -values and the influence of illumination on the SiO₂(Si)<Ti> electrode were observed after etching off the SiO₂<Ti> layer in HF acid, similarly as it occurred in the case with Al-implanted structures. In Fig. 5, the dependences $AJ(t)$ obtained for the Si<Ti>-Pt pair are shown. An essential influence of illumination on current generation owing to water decomposition in the absence of the external voltage between the electrodes ($V = 0$) is evident (curves I_d and I_L). The dependences $AJ(t)$ at $V = \pm 9.7$ V are similar to those obtained for the Si<Al>-Pt pair under the same conditions (Fig. 3), but the $AJ(t)$ -values for Ti-implanted structures are lower. For etched Si<Ti> structures, as well as for Al-implanted ones, a strong reduction of the $AJ(t)$ -values – owing to structure ageing (oxidation) – is observed. This is demonstrated by curves

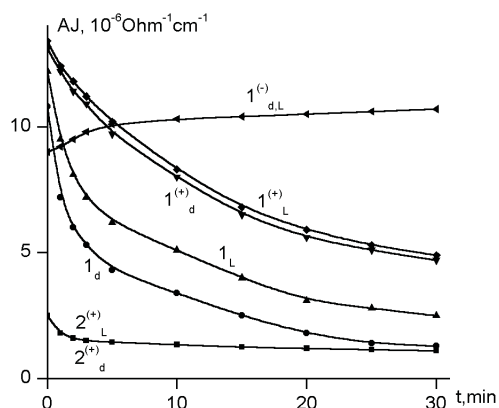


Fig. 5. Time dependences of water conductance for the electrode pair Si(Ti)-Pt after etching off the SiO₂(Ti) layer from the SiO₂(Si)(Ti) electrode. Curves I_d and I_L correspond to $V = 0$, and curves $I_d^{(+)}$, $I_L^{(+)}$, $I_{d,L}^{(-)}$, $\varrho_d^{(+)}$, and $\varrho_L^{(+)}$ to $V = \pm 9.7$ V on the Si(Ti) electrode. Curves $\varrho_d^{(+)}$ and $\varrho_L^{(+)}$ correspond to the aged surface. The subscript d stands for darkness and L for illumination. The AJ -values for curve $\varrho_L^{(+)}$ are larger by about 10% than those for curve $\varrho_d^{(+)}$

$\varrho_d^{(+)}$ and $\varrho_L^{(+)}$ measured 24 h after the earlier measurements (curves $I_d^{(+)}$ and $I_L^{(+)}$).

After etching off the SiO₂(Ti) layer, the Si(Ti) electrode in the Si(Ti)-Pt pair is an anode ($\varphi = 4.22$ eV), and Pt is a cathode. In the Si(Ti)-Yb pair, Yb is an anode, and Si(Ti) is a cathode. This circumstance gives rise to the change of the character of the measured $AJ(t)$ dependences for the pairs Si(Ti)-Pt and Si(Ti)-Yb, which can be well seen from Figs. 5 and 6, where the corresponding dependences $AJ(t)$ are exhibited.

4. Conclusions

1. After the implantation of Al and Ti impurities into SiO₂(n -Si) structures, the SiO₂(Si)(Al) and SiO₂(Si)(Ti) electrodes start to demonstrate a small (of the order of 10%) photosensitivity which manifests itself in the growth of the current between these electrodes and the Pt and Yb counterelectrodes at illumination, owing to water decomposition, $H_2O \rightarrow OH + H$, in this electrochemical system. In so doing, the positive voltage is applied to the SiO₂(Si)(Al) and SiO₂(Si)(Ti) electrodes, which makes them electron-depleted.

2. After etching off the implanted SiO₂(Al) and SiO₂(Ti) layers in HF acid, so that the implanted Si(Al) and Si(Ti) structures are formed, a substantial (of about 50%) influence of illumination on the current generation has been found. The current generation has been associated with the water decomposition in the

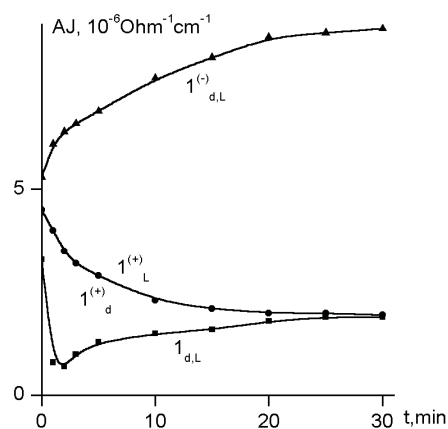


Fig. 6. Time dependences of water conductance for the electrode pair Si(Ti)-Yb. Curve $I_{d,L}$ corresponds to $V = 0$, and curves $I_d^{(+)}$, $I_L^{(+)}$, and $I_{d,L}^{(-)}$ to $V = \pm 9.7$ V on the Si(Ti) electrode. The AJ -values for curve $I_L^{(+)}$ are larger by about 10% than those for curve $I_d^{(+)}$

electrochemical systems Si(Al)-Pt and Si(Ti)-Pt in the absence of external voltage ($V = 0$).

3. If an external voltage ($V = \pm 9.7$ V) is applied across the Si(Al)-Pt and Si(Ti)-Pt systems that are immersed into distilled water, the growth of water-decomposition currents is observed; the growth takes place owing to the presence of strong electric fields emerging at impurity-induced structural inhomogeneities on the surface of Si(Al) and Si(Ti) electrodes. In this case, the illumination plays a smaller role in governing the current magnitude if $V = +9.7$ V, and has no effect if the electrodes are electron-enriched (the applied voltage $V = -9.7$ V).

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ВПЛИВ ОСВІТЛЕННЯ НА РОЗКЛАДАННЯ
ВОДИ НА КРЕМНІЄВИХ ЕЛЕКТРОДАХ,
ІМПЛАНТОВАНИХ ДОМІШКАМИ АЛЮМІНІЮ І ТИТАНУ

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Резюме

На термічно окислених зразках n -Si ($\rho = 4$ Ом·см), імплантованих домішками Al ($E = 75$ кеВ, $D = 1,15 \cdot 10^{16}$ см⁻²)

і Ti ($E = 125$ кеВ, $D = 7,6 \cdot 10^{15}$ см⁻²), використаних як електроди у дистильованій воді, досліджено розкладання води. Контрелектродами служили Pt або Yb. Вперше виявлено вплив освітлення Si(Al)- і Si(Ti)-електродів на струмоутворення з розкладанням води за відсутності зовнішньої електричної напруги ($V = 0$) між кремнієвим і контрелектродом, а також при прикладанні до кремнієвих електродів зовнішньої позитивної напруги ($V = +9,7$ В). Роль освітлення у зростанні темпу розкладання води зводиться до збагачення приповерхневої області кремнію електронами.