# Development of Silicon-Based Photoelements Containing Clusters of Nickel Atoms

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Abstract: A technology for producing nickel atom clusters in the volume of a silicon crystal lattice with controlled parameters has been developed. Solar cells based on silicon containing nickel atom clusters have been manufactured and their parameters have been determined. It has been established that the presence of nickel atom clusters in the lattice allows for a significant expansion of the spectral sensitivity region of silicon solar cells toward the IR spectrum to 4 μm. A new technological method for producing efficient solar cells (SC) with stable parameters and maximum efficiency has been proposed. Technology of creation of clusters of nickel atoms in the silicon crystal lattice with adjustable parameters was developed. Solar cells based on silicon containing clusters of nickel atoms were developed and their performances were determined. It is found that the presence of clusters of nickel atoms in the lattice allows to significantly broaden the spectral sensitivity region of the silicon cells toward the IR spectrum to 4 microns. A new technological method of manufacturing effective solar cells with stable parameters and maximum coefficient of performance has been revised.

## 1 INTRODUCTION

The currently existing manufacturing technologies and semiconductor materials used in the development of efficient solar cells (SC) with stable parameters and maximum efficiency have practically reached their limit. To further improve the main parameters of SC, it is necessary to use fundamentally new semiconductor materials or new physical phenomena.

The basis of modern solar photoenergy is made up of solar cells made of silicon. One of the reasons for the limitation of the efficiency of silicon solar cells is the impossibility of using the infrared (IR) region of the solar spectrum with $\lambda>1.2$ μm for photogeneration of charge carriers, and, as is known, the IR spectrum of the Sun with $\lambda=1.2\div3$ μm contains about 40% of the radiation power falling on the Earth's surface. Modern technology for the production of silicon solar cells and materials does not allow this issue to be successfully resolved. Also, the inability to use "extra" photon energy $\Delta E= h\nu- E$, leads to the effect of thermolysis, that is, its transformation into heat, which leads to heating of photocells and deterioration of their parameters. In photovoltaics, to reduce the effect of thermolysis and increase the absorption coefficient of UV in the visible part of the solar spectrum, so-called multi-cascade photocells have been developed on the basis of semiconductor compounds $A^{III}B^{V.}$ Multi-cascade photocells, although characterized by high efficiency, the technology of their manufacture, however, is quite complex and requires expensive equipment.

In this regard, semiconductors with clusters of impurity atoms are of great scientific and practical interest. This is primarily due to the possibility of targeted control of the fundamental parameters of semiconductor materials, as well as the discovery of unique physical phenomena in such materials, which make it possible to create a number of fundamentally new electronic devices on their basis [1]-[3]. If we take into account that clusters, depending on the nature of impurity atoms and the electron structure, can have metallic and semiconductor properties, and they can also have a sufficient magnetic moment, then the study of the physical properties of cluster-semiconductor microstructures is of particular interest. Since such structures can be obtained in the form of internal buried Schottky barriers and heterojunctions both on the surface and in the volume of the crystal with a sufficiently high density (N ~$10^5 \div 10^6$ cm$^{-2}$). The study of the electrical parameters of such structures allows us to reveal their still unknown facets and potential capabilities.

The aim of the presented work was to develop a technology for manufacturing photocells with clusters of nickel atoms and to study their parameters.

Recent studies have shown that the introduction of nanoscale impurity clusters into semiconductor materials can significantly modify their optical and electrical properties. In particular, transition metal clusters may create intermediate energy levels within the forbidden band gap, thereby extending the spectral response of silicon-based photovoltaic devices into the infrared region.

Although considerable progress has been achieved in the development of high-efficiency silicon solar cells, the utilization of infrared radiation remains a major challenge. Various approaches, including quantum dots, impurity photovoltaics, and multijunction structures, have been proposed. However, many of these technologies require complex fabrication processes and expensive materials.

Therefore, the development of silicon-based photovoltaic structures containing nickel atom clusters represents a promising approach for increasing spectral sensitivity while maintaining the technological simplicity of conventional silicon processing.

# 2 MATERIALS AND METHODS

The clusters were formed by doping silicon with nickel using our own technology, the so-called low-temperature and step-by-step diffusion [4]. Industrial single-crystal silicon of both n-type conductivity with phosphorus concentration ($N_P = 5 \cdot 10^{13}$, $4 \cdot 10^{14}$, $2 \cdot 10^{15}$ cm$^{-3}$) and p-type conductivity with boron concentration ($N_B = 10^{15}$, $4.5 \cdot 10^{16}$, $2 \cdot 10^{17}$ cm$^{-3}$) was used as the initial material for the studies. This choice of material was due to the establishment of patterns of formation and parameters of clusters depending on the type and concentration of impurity atoms. The state of clusters and their density in the samples were studied using an MIK-5 infrared microscope.

A typical MIK-5 infrared microscope works based on the interaction between infrared light and the internal structure of semiconductor materials. Silicon is also partially transparent in the near-infrared spectral region, allowing for infrared radiation to enter into the crystal volume and expose subsurface structural inhomogeneities not visible under optical microscopy. Differences in infra-red absorption, reflection and scattering due to accumulation of impurities, defects and clusters creates contrast on the recorded image, enabling internal structures to be imaged.

In this study, we utilize an infrared microscope (MIK-5) to examine the formation, distribution and self-organization of nickel clusters in silicon. As cluster-containing regions have different optical properties to the surrounding silicon matrix, nickel clusters are therefore observed as unique contrast areas in infrared images. It allows to probe the presence, size, density, spatial distribution and ordering (or not) of obelisks in the crystal volume. This makes infrared microscopy a non-destructive method to study cluster-semiconductor structures and mechanisms of impurity self-organization in silicon.

As the results of the studies showed, the state and density of clusters are practically independent of the type and concentration of the initial impurity atoms but mainly depend on the doping conditions. The main part of the introduced nickel atoms remains in the electroneutral state and is not located in the lattice nodes. Clusters of nickel atoms are observed in all alloyed samples. With increasing diffusion temperature, the density of clusters increases, and their size decreases accordingly. It was found that the main parameters of nickel clusters can be controlled in a wide range by changing the conditions of additional annealing. Additional heat treatment at temperatures of T = 600-1000 °C leads to significant changes. Depending on the annealing time, not only an increase in the size of the clusters is observed, but their ordering also begins, i.e. they are collected in certain directions and form chains.

The study of the state and distribution of clusters in the samples after step-by-step grinding by 50 μm to the middle of the sample thickness showed that the clusters are distributed uniformly throughout the entire volume of the sample. Figure 1 shows a photo of nickel clusters and their state in the silicon crystal lattice. In some samples, cluster loops appear in different crystallographic directions (Fig.2).

Comparison of the dynamics of formation and state of clusters of Ni impurity atoms in samples doped both in evacuated ampoules and in air showed that there are practically no significant differences, i.e. it is possible to dope silicon wafers of different diameters with nickel. This gives full grounds to assert that by controlling the diffusion temperature, cooling rate, time and temperature of subsequent additional low-temperature annealing, it is possible to control the density, size and distribution of clusters of nickel impurity atoms.

Infrared Micrograph of Nickel Clusters in the Silicon Crystal Lattice After Diffusion and Thermal Treatment (1) The picture captured by the MIK-5 infrared microscope shows that nickel atoms are not randomly scattered in the volume of crystals. Instead, they often coalesce into small clusters at the nanoscale or microscale. This behavior is believed to be attributed to the lowering of free energy of crystal lattice and interaction between impurities atoms and intrinsic crystal defects. These clusters show that nickel atoms are sufficiently mobile during thermal treatment to diffuse and segregate in the energetically favorable regions of the silicon matrix.

One of the prominent features in Figure 1 is the partial ordering and alignment of clusters along favored crystallographic directions. This phenomenon suggests that self-organization processes in the silicon lattice take place. The ordered arrangement of nickel clusters, along with the pairwise distance distribution functions and thus an unambiguous assignment of Long-range interaction type interactions mediated via elastic strain fields and defect structures. These self-organized cluster systems can largely impact on the electronic properties of silicon due to formation additional localized energy levels and inner potential barriers and can promote these high photoelectric and optical features of these hetero structures.

Looped formations created by nickel clusters within the silicon crystal are seen in infrared microscopic images in Figure 2. In this case, as seen in Figure 1, the clusters are ordered linearly; however, here they are closed or partially closed. Such loop structures show that impurity atoms are better spatially organized, and they mirror complex diffusion-aggregation-defect interaction of atoms under the influence of thermal treatment [1].

Modeling of viscous clusters should provide interpretation of the processes responsible for formation of cluster loops, which may be related to relaxation and redistribution of internal mechanical stresses, as well as interaction of nickel atoms with dislocations and other extended crystal defects. Physically from this perspective, these self-organized structures can be considered as effectively a string of localized electronic centers that influence charge carrier transport and recombination. These ordered loop-like configurations additionally indicate that unlike the random precipitation process this nickel clusters are formed through a self-organization mechanism.

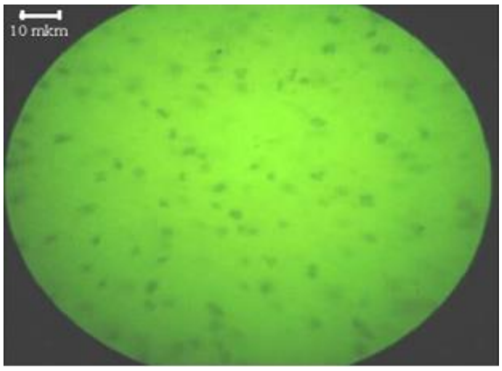


Figure 1: Ordering of nickel clusters in silicon.

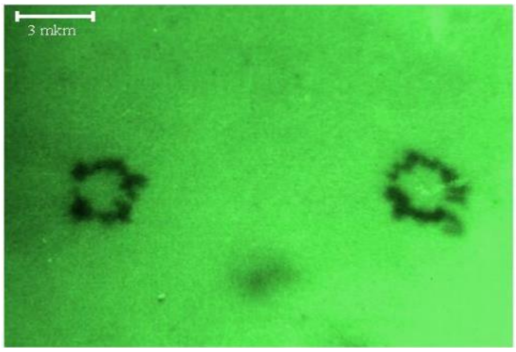


Figure 2: Loops consisting of nickel clusters.

This category of structures has a great promise in the design of improved silicon-based optoelectronic and photovoltaic devices with broader spectral sensitivities [2].

The elemental composition of the clusters was studied using a Jeol-8800R microprobe analyzer. It was found that the clusters contain mainly silicon atoms (97-98%) and nickel (2-2.5%), as well as a very small amount of oxygen, i.e. the resulting clusters can be considered as a solid solution of $Si_{1-x}Ni_x$ .Therefore, it is of interest to study the volt-ampere characteristic of the Ni -silicon cluster atom structure.

Ni -silicon cluster atom structures, a special setup with a tungsten microprobe. The thickness of the microprobe tip was less than 0.7 µm. The silicon surface measuring 4 mm x 4 mm was scanned in the x and y directions, and the current-voltage characteristics of different sections were recorded. Figure 3 shows the current-voltage characteristics of the Ni -silicon cluster atom structures based on p-type silicon.

## 3 RESULTS AND DISCUSSION

The current-voltage characteristic of such structures has an asymmetrical dependence of the current on the polarity of the applied field, i.e. it has rectifying properties, while it should be noted that in such structures the reverse current is very small ( $J_s$<$10^{-6}$ A) and does not depend on the applied voltage, i.e. it has a current-voltage characteristic characteristic of an ideal metal-semiconductor contact. The rectification coefficient $K = I_{pr} / I_{obr}$ of this structure, depending on the applied voltage, varies in the range of 80-150.

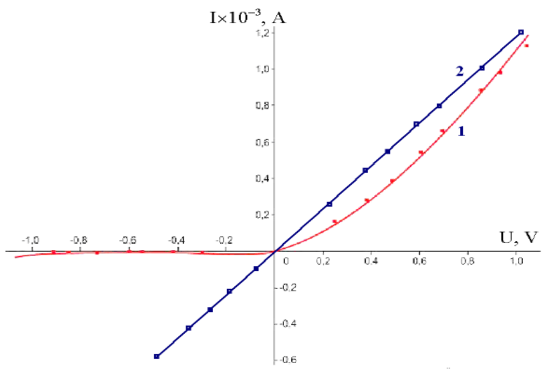


Figure 3: Current-voltage characteristics of nickel cluster-silicon microstructures.

The I-V characteristic of silicon containing clusters of Ni atoms from a sample-as well as the spatially resolved analysis of other regions free from clusters is illustrated in Figure 3 Curve 1 corresponds to the nickel cluster-silicon microstructure, and curve 2 is the electrical behavior of structures with no measured cluster formations in silicon matrix. The stark difference in the two curves conclusively shows that nickel clusters lead to a local alteration of silicon's electronic properties. In the area presenting clusters, the current depends on applied voltage nonlinearly, which is typical for creating a micro barrier metal-semiconductor. The analogous observed behavior indicates that nickel clusters serve as localized conductive centers able to generate internal potential barriers in the silicon crystal [3], [4].

The shape of the current-voltage characteristic with asymmetry and suppression of reverse current point to Schottky-type micro junctions patterns formed at the cluster-silicon interface. Employed micro barriers not only ensure directional transport of carriers but also have a great impact on the separation and collection of photogenerated charge carriers. The acquired results prove that for nickel clusters it is not just structural inhomogeneities but serves as the site of formation of electrically active areas deep within the crystal. Therefore, as a result of this process, self-organized nickel clusters can play an additional role in increasing the efficiency of photoelectric conversion processes and may well be responsible for expanding the spectral sensitivity of silicon-based photovoltaic structures into the infrared region.

As the study of the current-voltage characteristics of the nickel atom cluster - silicon structures based on the p-type material showed, it has a character similar to the n-type structures. But their difference is the value of the forward current, which is almost 1.5-2 orders of magnitude greater than in the n-type structure. Thus, the current- voltage characteristics of the Ni - silicon cluster atom structures, regardless of the initial concentration and type of silicon, have rectifying properties, but with different values of the forward and reverse current. These results give grounds to assume that a metal-semiconductor structure (Schottky barrier) is formed in this case [5]. have calculated the value of the potential barrier of Schottky diodes based on the values of the reverse current [6] of cluster-silicon structures depending on the type and concentration of impurity atoms of the initial material:

$$J_s = AT^2 exp\left(-\frac{\phi_K}{kT}\right). \quad (1)$$

The value of which for cluster- p -silicon structures is $\varphi_k$ = 0.6 ÷0.65 eV, and for cluster-n-silicon structures it is $\varphi_k$ = 0.6 0.8 eV. Very small values of the reverse current and a weak dependence on the applied reverse voltage give grounds to assume that ÷Schottky diodes based on cluster- Si have more perfect contact areas. This is apparently due to the absence of various defect structures and an oxide layer in the contact area, which are present in conventional Schottky barriers [7].

Study of photoelectric properties of microdiodes Schottky showed that such structures have a high photovoltage at room temperature and, depending on the cluster parameters (size, depth, etc.), it is $V_{xx}$ ~100 ÷150 mV (Fig. 4). These data show that in Si samples with a cluster density of N ~$10^5$÷$10^6$ $cm^{-2}$, by connecting them, it is possible to obtain an abnormally high photovoltage [8]-[10].

The photocells were made in the form of parallelepipeds with dimensions 0,5 смx 1 смand a thickness of 380 µm. The p-n junction of the photocells was formed by boron diffusion using boron nitride plates in the case of n-type samples or by phosphorus diffusion from a surface source in the case of p-type samples. The surface concentration of boron atoms was Ns = 10 $^{19}$cm $^{-3}$. The depth of the p-n junction was about 1 μm. The current-collecting contacts were created by thermal spraying of nickel through a mask in a vacuum, which were tinned by dipping in POSK-50-18 solder. No antireflective coating was used [6], [11].

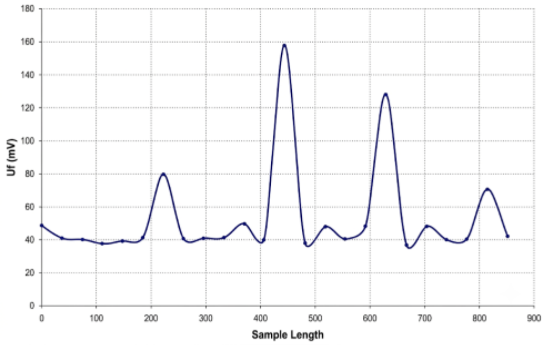


Figure 4: Photo-EMF of the structures of cluster atoms Ni - silicon

To carry out measurements under identical conditions AM 1.5 was used a solar radiation simulator, manufactured on the basis of an incandescent lamp with a correction filter. To study the spectral characteristics of the manufactured photocells with nickel atom clusters, a setup based on the IKS-21 monochromator was specially developed and manufactured, which ensured measurements of the voltage and current of the photocells in the wavelength range from 0.4 to 8 μm. The parameters of the photocells manufactured on the basis of the KEF 2 material after the formation of nickel atom clusters are given in Tables 1 and 2.

Table 1 summarizes the principal photovoltaic parameters of silicon solar cells fabricated from KEF-2 material after different annealing conditions responsible for the forms of nickel atom clusters. It is evident from the results that the cluster size highly relies upon the annealing temperature. For the case of high annealing temperatures (1000-1100 °C), relatively small clusters with dimensions ranging from 1 to 5 μm are formed, and at reasonable annealing temperatures (600-800 °C) the size of clusters increases reaching sizes of about 20-30 μm. On the other hand, UOC remains rather stable over all studied cases varying in a range of 480-507 mV suggesting that not only nickel inclusion neither essentially worsen p-n-junction properties fabricated cells [12]-[14].

The short-circuit current density (Isc) exhibits a more pronounced effect. The maximum value reaches to 45.7 mA/cm² after annealing at 900 °C, which is more than two times higher compared with the value of the control sample (20.5 mA/cm²). This result suggests that the formation of these nickel clusters under the favorable thermal treatment conditions significantly improves both generation and collection of charge carriers. Nickel clusters lead to the emergence of new discrete states in forbidden zone, which increases long-wavelength radiation absorption and transporting existing carriers within silicon matrix, that nicely elucidates enhanced photocurrent values. Consequently, a favorable annealing temperature of ~900 °C can be noted as optimal to acquire silicon solar cells with improved photovoltaic properties [15]-[17].

The results presented in Table 2 demonstrate that the spectral sensitivity of silicon photocells containing nickel atom clusters strongly depends on the wavelength of the incident radiation. The maximum sensitivity is observed in the visible spectral region, reaching 991.2 μA/mW at a wavelength of 0.6 μm. High sensitivity values are also recorded at wavelengths of 0.45-0.9 μm, which indicates efficient photogeneration and collection of charge carriers in this region. As the wavelength increases beyond 1 μm, the sensitivity gradually decreases, which is typical for conventional silicon-based photovoltaic devices due to the limitation imposed by the silicon band gap.

Table 1: Influence of annealing temperature and nickel cluster size on the photovoltaic parameters of silicon solar cells.

| Additional annealing at a temperature of $^{about}$ C. | Cluster size (μm) | $U_{x.x}$ (mV) | $I_{к.з}$ (mA / cm²) |
|---|---|---|---|
| 1100 | 1-2 | 480 | 20.9 |
| 1000 | 2-5 | 482 | 21.4 |
| 900 | 2-5 | 498 | 45.7 |
| 800 | 2-20 | 506 | 28.1 |
| 700 | 2-30 | 503 | 20.2 |
| 600 | 2-30 | 500 | 20.4 |
| Control | | 507 | 20.5 |

Table 2: Spectral sensitivity of photocells manufactured on the basis of KEF 2 material after the formation of nickel atom clusters.

| Wavelength μm | 0.43 | 0.45 | 0.5 | 0.6 | 0.9 | 1 | 1.05 | 1,2 | 1.42 | 1.85 | 2.25 | 2.65 | 3.05 | 3.45 | 3.85 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I, μA/mW | 240 | 562.9 | 685.1 | 991.2 | 751.4 | 231.8 | 55.6 | 4.3 | 0.6 | 0.6 | 0.99 | 4.4 | 16.74 | 13.25 | 11.6 |

At the same time, an important feature of the obtained results is the preservation of measurable photosensitivity in the infrared region up to 3.85 μm. Although the photocurrent decreases significantly after 1.2 μm, non-zero sensitivity values remain in the range of 1.42-3.85 μm. In particular, the sensitivity increases again at wavelengths of 2.65-3.85 μm, reaching 16.74 μA/mW at 3.05 μm. This behavior confirms that nickel atom clusters introduce additional energy states within the silicon band structure, enabling the absorption of lower-energy infrared photons. Consequently, the formation of nickel clusters leads to a substantial extension of the spectral response range of silicon photocells and creates favorable conditions for improving the overall efficiency of photovoltaic energy conversion.

# 4 CONCLUSIONS

This work has developed a process for the formation of nickel atoms clusters into silicon crystals, and studied their effects on the structure, electrical and photoelectric properties of silicon-based solar cells. Infrared microscopy studies carried out in a MIK-5 infrared microscope have proved that therein nickel atoms create clusters spread within the crystal volume with striking self-organization phenomena. Images obtained from these experiments showed that the clusters did not simply form and disappear randomly but were observed to arrange along certain preferred crystallographic directions and create loop-like structures, suggesting far ranging interactions between impurity atoms and crystal defects.

Electrical measurements indicated that the Ni cluster-Si microstructures have Schottky-type rectifying micro barrier characteristics. The current-voltage characteristics proved the ohmic nature of internal metal-semiconductor interfaces that can significantly affect charge carrier transport and separation processes. The photovoltaic properties of the fabricated solar cells can be strongly dependent on both annealing conditions and cluster dimensions. A short-circuit current density of 17.8 mAcm-2 was achieved at an annealing temperature of around 900 °C, which is optimal for cluster formation and carrier generation.

We found that the spectral sensitivity measurements revealed a considerable enhancement of silicon photo response in visible light region and beyond due to incorporation of nickel atom clusters. In contrast to the conventional silicon solar cells, having a photosensitivity wavelength range up to 1.1-1.2 μm, the structures developed in this study exhibit measurable photosensitivity also at infrared wavelengths up to ≈4μm, which is well associated with appearance of additional energy states arising from face-centered nickel clusters [18]. This allows for absorption of low-energy photons and assists carriers' generation leading to effective photocurrent.

The results reported here demonstrate that self-organized nickel atom clusters embedded in silicon could provide exciting new materials for next-generation photovoltaic devices with enhanced spectral responsiveness. These structures may be an attractive alternative to high cost multijunction solar cells based on $A^{III} B^{V}$ and $A^{II} B^{VI}$ semiconductor compounds, while preserving the low production cost by simpler fabrication technology and compatibility with established silicon processing equipment.

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