

Effects of using either boron-phosphorus dopants or gallium-arsenic dopants in silicon photovoltaic cells

Anson Moorey

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Abstract

Increasing the efficiency of renewable electricity sources is a significant endeavor in modern society. In the design of photovoltaic cells, the chemical structures that generate electron flow are the primary determining factors of efficacy. In the context of silicon wafer photovoltaic cells, is there a benefit or a drawback to changing the common p-type and n-type dopants, boron and phosphorus, to gallium and arsenic? The primary disadvantage of boron is a lower recombination time of charge carriers in the presence of B_5O_2 in Czochralski silicon. This lowers the efficiency of the photovoltaic cell. Empirical data from other scientific literature is assessed to draw conclusions. It is concluded that conditionally, boron and phosphorus are more efficient. With a boron dopant, to have photovoltaic efficiency equal to that of gallium would require alternative methods of silicon crystal structure growth that do not produce an oxygen concentration any higher than 1ppm, or to modify B_5O_2 to a "regenerated" inactive state. Furthermore, electron drift is slower in arsenic-doped silicon than in phosphorus-doped silicon, leading to a lower efficiency when using arsenic.

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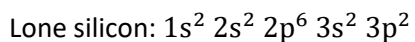
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Introduction

Increasing the efficiency of renewable electricity sources is a significant endeavor in the support of modern society. This includes solar panels made up of photovoltaic cells. In the design of photovoltaic cells, the chemical structures that generate electron flow are the primary determining factors of efficacy. In the context of silicon wafer photovoltaic cells, is there a benefit or a drawback to changing the common p-type and n-type dopants, boron and phosphorus, to gallium and arsenic?

Chemistry Background Information

A semiconductor silicon wafer is a crystal structure in which each silicon atom bonds with 4 other silicon atoms. Since a lone silicon atom has 4 valence electrons, when four of them are bonded to one of them, every covalent bond will have 2 electrons. Due to this, every atom will be stable with a full valence level of 8 bonding electrons.



These are four sigma (σ) bonds. As displayed in Figure 1, three are caused by three local p orbitals overlapping with foreign p-orbitals. The last bond is caused by the local s orbital overlapping with a foreign s orbital.

Figure 1: *The electrons and σ bonds made by a silicon atom in a crystal structure.*

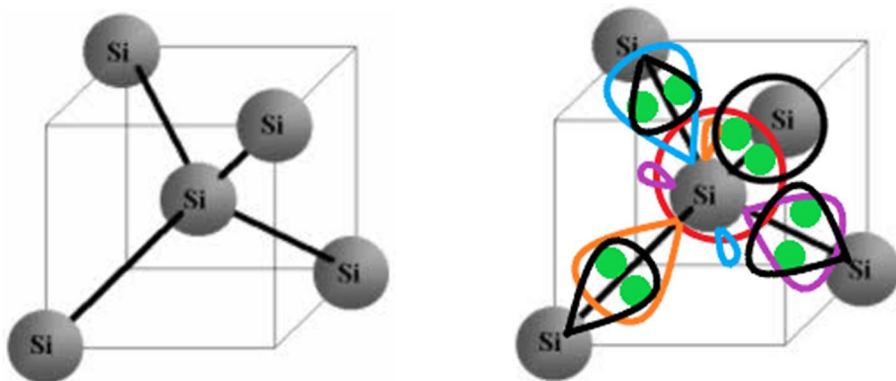


Image Source: Annotated version of (Xiao, n.d.)

Note: The larger circles are silicon atoms, and the small points represent the distribution of the center silicon's electrons within its outlined s and p orbitals as they bond with the s or p orbitals of the surrounding silicon atoms.

In this state in Figure 1, the electron demand to fill valence orbitals is met. If some of the atoms in the crystal structure originally had less than four valence electrons to contribute, there would be an electron deficiency, known as a p-type (positive) material. If it had more than four electrons, there would be an electron surplus, known as an n-type (negative) material. For conciseness, a region of electron deficiency is referred to as a hole.

Photovoltaic Cells

When placing a layer of p-type semiconductor in parallel contact with a layer of n-type semiconductor, the boundary between layers is referred to as the p-n junction. Surplus electrons will recombine with adjacent holes along this boundary (Figure 2). After this deficiency is satisfied and recombined, there becomes a neutral “depletion zone” along the p-n junction. When photons collide with the crystal structure, electrons jump to higher energy levels to the extent that they overcome the attraction to atomic nuclei. For this reason, there becomes an extra electron and an extra hole. Electrons and holes are charge carriers. In an area of material, the more abundant charge carrier is the majority carrier and the less abundant is the minority carrier. For example, in a p-type region, the minority carriers are electrons.

Figure 2: *Diagram of the interactions between n-type and p-type layers.*

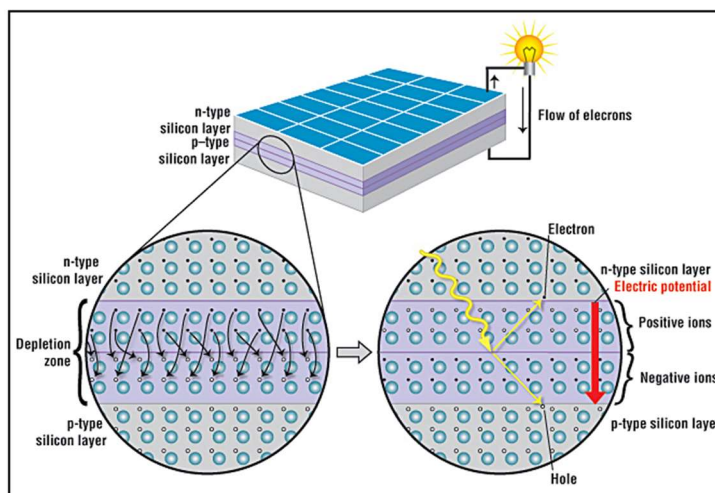


Image Source: (Fernandez, 2013)

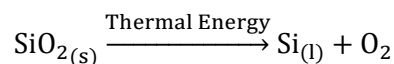
From one side of the depletion zone to the other, there is an electric field caused by cations and anions. When extra electrons are freed by photon collision, the electric field restricts the extra electrons from crossing into the p-type zone, and it keeps the extra electrons from immediately returning to their hole after jumping. By using a conductive wire to connect the two layers, a current is generated by the potential difference between the p-type and n-type layers.

Dopants

A dopant is an element that is added very sparsely to the silicon semiconductor, but it vastly changes the electrochemical properties of the material. Adding a dopant to silicon is how n-type and p-type materials are created. Most commonly, boron and phosphorus are used for p-type and n-type doping. In space station and military technology, more costly gallium and arsenic are used for higher efficiencies. According to Yamaguchi et al. (2016), GaAs three-junction photovoltaic cells reached 44.4% efficiency in a lab setting.

The Czochralski Method

The Czochralski method (Cz) is a method of crystal growth used for silicon semiconductors. On the end of a rod, a crystal seed contacts the surface of melted silicon in a silica (SiO_2) crucible. During this process, the walls of the crucible dissolve into the sample, causing oxygen impurities (Global Wafers Japan, n.d.). Silicon crystal structures formed by this Cz process include an oxygen concentration, $[\text{O}_i]$, of around $10^{18} \text{ atoms cm}^{-3}$ (Casse et al., 1999).



The rod rotates and slowly rises from the molten surface. As the silicon rises out of the crucible, it cools. As a result, the cylindrical silicon crystal is formed hanging from the rod. This cylinder can then be cut and polished into a wafer. For a doped silicon crystal, the dopant element is simply dissolved into the molten silicon prior to beginning the process.

The magnetic Czochralski (MCz) method is a modified version in which a magnetic field is applied perpendicularly to the melted silicon surface. Since the melted silicon can conduct electricity, this magnetic field generates a force in the flow of the silicon. This modified flow can be used to change some properties of the crystal (Global Wafers Japan, n.d.). This magnetic technique can be used to reduce the amount of oxygen impurities.

Carrier Lifetime and the Boron-Oxygen Complex

Carrier lifetime is the average time of a minority charge carrier taken before recombining. To optimize energy output of the system, recombination must be avoided. A significant issue facing boron-doped photovoltaic cells is the light-induced degradation. This is a decrease of efficiency over time attributed to boron-oxygen defects.

An oligomer is a molecule made up of a few smaller molecules (monomers). Unlike a polymer made of thousands of monomers, an oligomer is only made of a few and therefore is far more impacted by individual monomers. The term dimer refers to an oligomer made up of two monomers.

More specifically, a boron-oxygen complex is a substitutional boron atom and an oxygen dimer (two interstitial oxygen atoms), B_2O_2 (Markevich et al., 2019). A substitutional atom is one that is taking the place of another type of atom. In this case, a boron atom is taking the place of a silicon atom in the silicon structure. An interstitial atom is one that is positioned in a non-regular place between atoms in an array of regularly positioned atoms. In this case, there are two interstitial oxygen atoms present in non-regular positions that change the pattern within the silicon structure (Figure 3).

Figure 3: *Forms of the B_2O_2 oxygen complex*

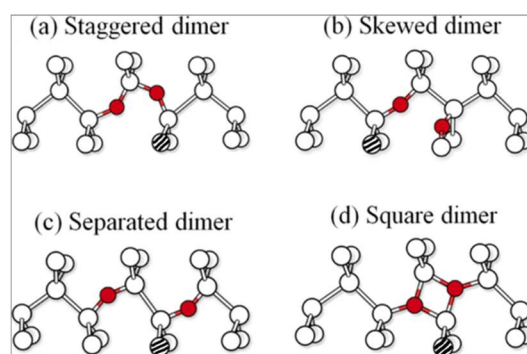


Image Source: Annotated version of (Yu, n.d.)

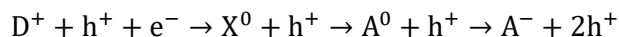
Note: White nodes are silicon, solid red nodes are oxygen, and striped black nodes are boron.

In a boron-doped p-type semiconductor with an oxygen impurity, this boron-oxygen dimer complex, B_2O_2 , is present inside the silicon structure. This boron-oxygen complex has been the focus of photovoltaic research for decades, yet some of the exact mechanisms that cause its light-induced degradation have been somewhat elusive. This boron-oxygen complex will have its own energy levels different than the rest of the silicon structure, causing electrons to become trapped in the complex, unable to generate current. This is why the light-induced degradation is asymptotical, because eventually all boron-oxygen complexes will have accepted the maximum number of charge carriers that they can. After this initial quicker degradation of efficiency, the rate of change of efficiency approaches zero as it reaches an asymptote. This forever remains as the efficiency unless external factors like thermal effects are applied.

Primary Data from Scientific Literature

States of Interstitial Structure

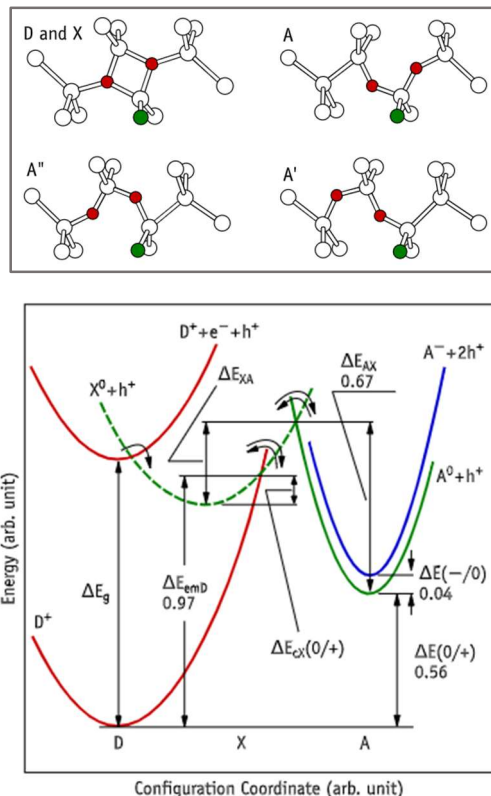
In boron-doped silicon, the material is p-type, so the minority carriers are electrons. Injection of a minority carrier can occur either due to a photon collision or due to an external voltage. According to Markevich et al., upon injection of a minority carrier, this B_sO_2 complex changes from the D^+ state into the A^- state and two holes (h^+) are emitted. The D and A states refer to deep donor and shallow acceptor respectively. The A^- state is known as the “degraded” state. These are the intermediate stages that ultimately reach the degraded state:



To anneal means to treat the semiconductor with heat to reset or perfect the crystal structure. By thermally increasing the velocity of bonded electrons, they gain the opportunity to redistribute. This changes the state back to D^+ . Thus, the D^+ state is also known as the “annealed” state.

The relative energy levels between states are displayed in a configuration coordinate diagram by Markevich et al. (Figure 4). As seen in the configuration coordinate diagram, local minima are indeed metastable, but D^+ is always the most stable state of the B_sO_2 complex.

Figure 4: D, X, and A states of the boron-oxygen complex.



Images Source: (Markevich et al., 2019)

Note: In the diagram, white molecule nodes are silicon, solid red nodes are oxygen, and solid green nodes are boron.

According to experimental data by Herguth et al. (2008), after being illuminated for a length of time, the current density in boron-doped Cz silicon rises to a saturation point, then declines (Figure 5). According to Wolny et al. (2017), current density does correlate with $[O_i]$ concentration and efficiency. As postulated by Herguth et al., this decline is a regeneration process leading to some form of “regenerated” state that is inactive in the context of charge carrier recombination. This is considered a third state in addition to the annealed and degraded states. Therefore, the complex-caused recombination activity can be eliminated by regenerating the complexes to this state. This can eliminate light-induced degradation caused by boron and oxygen.

Boron and Gallium

In the primary data by Schmidt et al. (Figure 6), bulk carrier lifetimes (τ_b) are lower with the boron dopant than with the gallium dopant. To gather this data, Schmidt et al. used Czochralski (Cz) silicon wafers under halogen lamp illumination with an intensity of 350 mW/cm^2 . For dopants of different elements and resistivities, they have measured the bulk carrier lifetimes over time spent exposed to light. These four different dopants are $10 \text{ } \Omega\text{cm}$ gallium, $10 \text{ } \Omega\text{cm}$ boron, $1.5 \text{ } \Omega\text{cm}$ boron, and $1.0 \text{ } \Omega\text{cm}$ boron.

This graph axis is displayed on a logarithmic scale, so the difference in bulk carrier lifetime between gallium and the closest boron is significant, around $100 \mu\text{s}$. Although $10 \text{ } \Omega\text{cm}$ boron does have a longer bulk carrier lifetime before 60 minutes, if illuminating longer than 120 minutes, τ_b with $10 \text{ } \Omega\text{cm}$ boron is approximately 16.7% worse than with $10 \text{ } \Omega\text{cm}$ gallium. As stated earlier, a quicker carrier lifetime is quicker recombination, and is therefore a source of energy loss and efficiency loss.

Figure 5: Current density over time

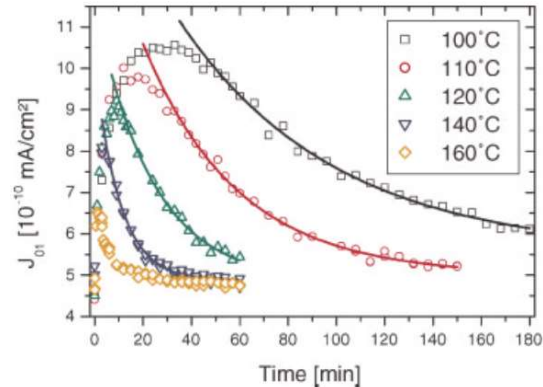


Image Source: (Herguth et al., 2008)

Figure 6: Bulk carrier lifetimes over time

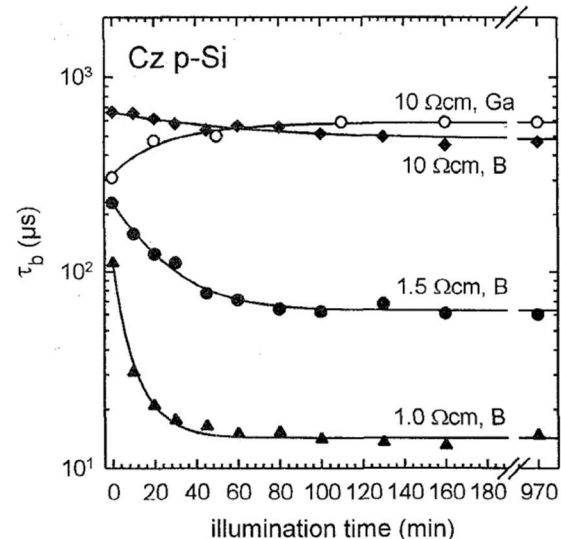


Image Source: (Schmidt et al., 1997)

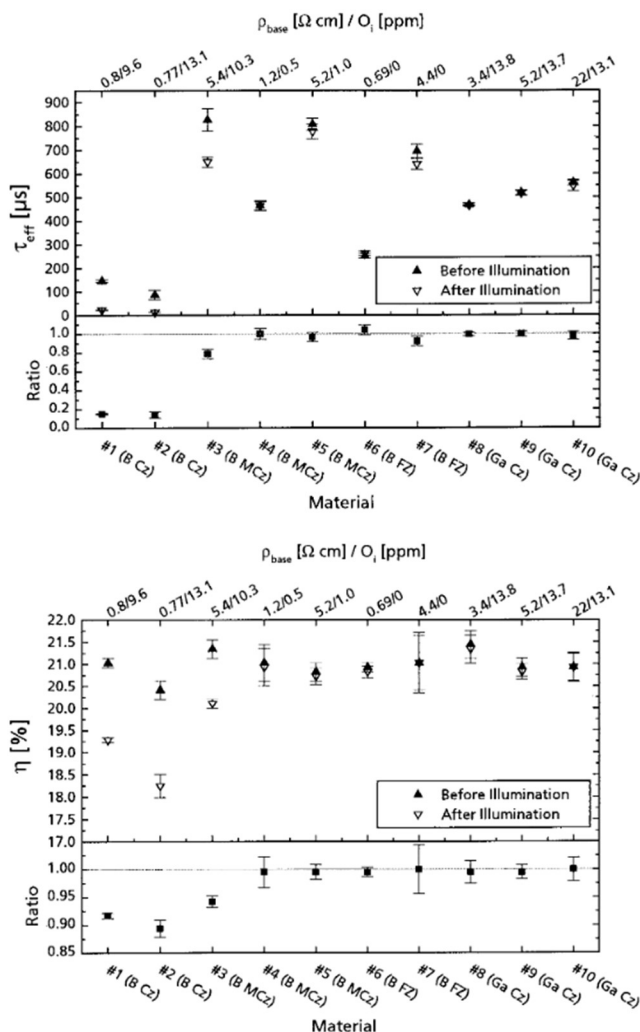
In addition to the disadvantages of boron, what are the advantages of gallium? There may not be any. Before and after 30 hours of 100 mW/cm^2 illumination, Glunz et al. measured charge carrier lifetime and efficiency (Figure 7). They did this for gallium and boron, with different crystal growth techniques. The resulting ratio between initial and final values remained 1 for most materials tested, including materials with boron (Figure 7). Only boron materials with $[O_i]$ concentrations greater than 9.5ppm were severely impacted by illumination, certainly due to the boron-oxygen complexes. Boron materials with $[O_i]$ concentrations less than or equal to 0.5ppm, and all gallium materials, had almost no impact by illumination.

Indicated on the materials axis on the data from Glunz et al., the only crystal growth techniques that all had almost no change of efficiency are boron FZ (boron-doped float-zone silicon) and all gallium trials (which are all Cz silicon). All boron trials that used the Cz technique performed poorly by having too much oxygen, and one type of MCz boron also performed poorly for having too much oxygen.

Phosphorus and Arsenic

Masetti et al. (1983) have empirical evidence that when using arsenic as a dopant, the electron mobility in the semiconductor is lower than when phosphorus is the dopant. Electron mobility is the electron drift (velocity) per unit electrical field strength. To affect the ability of a charge carrier to move through a field will undoubtedly influence the electrochemically induced current. Therefore, use of arsenic as an n-type dopant would decrease efficiency.

Figure 7: Primary data of both charge carrier lifetimes and efficiency for different materials



Images Source: (Glunz et al., 1999)

Source Evaluation

Methodology of Choosing Source Literature

To find relevant and valuable primary and secondary data sources, Google Scholar is used. Judgement of a source to be included is based upon relevancy to the research question and by the perceived degree at which it can justify its own claims.

Reliability of Experiments in Literature

Schmidt et al. used light-biased microwave-detected photoconductance decay (MW-PCD) measurements. According to Basore and Hansen (1990), MW-PCD is indeed a reliable technique if interpreted correctly. The silicon wafers were annealed at 350°C for 10 minutes. This can allow for electrons trapped by the boron-oxygen complexes to escape back into the regular flow, temporarily resetting any prior light-induced degradation by annealing back to the D^+ stage. This is a beneficial technique to conduct immediately before an experiment because it resets the properties of the material as constants in the experiment.

Markevich et al. used “DLTS [deep-level transient spectroscopy] spectra and capacitance–voltage curves of the diodes on boron-doped Si” to identify “fingerprints” of complexes. This allows the control of other complexes like hydrogen-, iron-, and copper-related defects. They claim that due to this fingerprinting data, they are confident that all resulting observations are only related to boron-oxygen complexes rather than any other defects.

Herguth et al. annealed their samples at 200°C for 30 minutes in the dark to keep the initial properties constant. As described before, this initial state can allow for others to attempt reproduction of results in a controlled manner.

Glunz et al. used an infrared Fourier transform spectrometer to measure interstitial oxygen [O_i] concentrations. They calibrated following DIN 50438 standards. For charge carrier lifetime measurements, an extensive RCA clean and 425°C annealing process was undergone on all samples before the experiment. Again, MW-PCD is used for measurements, and there is also a constant 0.5-suns white bias light to maintain consistent MW-PCD measurement.

Acceptance by the Scientific Community

Google Scholar displays analytics of the number of scholarly articles or documents that have cited a particular work. This can be used to estimate the impact that a publication has made in the

scientific community. Schmidt et al. (1997) was cited 344 times, Markevich et al. (2019) was cited 25 times, Glunz et al. (1999) was cited 166 times, Herguth et al. (2008) was cited 213 times, and Masetti et al. (1983) was cited 1133 times. Year of publication must be considered when assessing number of citations that a publication has received, but overall, these are reliable values. Therefore, the phenomena of light-induced degradation, general efficiency values, and relations between $[O_i]$ and charge carrier lifetime are commonly accepted and are proven by impactful empirical evidence.

Conclusion

Overall, when using the Czochralski method for silicon growth, using boron as a dopant can directly decrease efficiency. In this case, compared to boron, gallium is a robust choice of dopant due to its lack of light-induced degradation. Although, if a silicon-growth technique is used that does not result in high oxygen concentrations, then boron can be used to the same effect as gallium. To use arsenic rather than phosphorus to dope the n-type material would negatively influence the resulting current, and so would lower the efficiency. For this reason, phosphorus is the superior choice.

Beyond chemistry, other factors will certainly determine effectiveness of solar panels in the commercial market. Cost, availability, transportation conditions, and exposure safety are all significant factors in the decision between boron-phosphorus pairs and gallium-arsenic pairs. In addition to the chemical disadvantages of arsenic, it is also more toxic than phosphorus (World Health Organization, 2022).

To conclude, gallium and arsenic would be the inferior choice due to the lower drift velocity of charge carriers in arsenic doped silicon. Boron and phosphorus would be more efficient, assuming that either float-zone (FZ) silicon is used, or the Czochralski (Cz) silicon has been regenerated to an inactive state.

Extension

Opportunity for extension of research is boundless. Similar analysis could be conducted on other dopant elements. Any impact caused by atomic radii when using elements of lower periods could be analyzed. Further research could be undergone into the “slow” and “fast” processes of light-induced degradation (Bothe & Schmidt, 2006), or into the supposed theory that these two processes are a single defect (Hallam et al., 2016). Finally, experimental data could be gathered by oneself for more control of what kinds of data can be measured. For example, to find more relevant data regarding the direct impact of phosphorus.

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