EVALUATION OF AGING EFFECTS OF ZINC OXIDE ON THE OPTICAL PROPERTIES OF POROUS SILICON-ZINC OXIDE HETEROJUNCTION PHOTODETECTOR DEVICE

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Abstract: Porous silicon is very important for integrated technology because of its many superior properties, such as suitability for mass production, easy and controlled production, and adjustable electrical and optical properties. Semiconductors with metal oxides, such as indium oxide, indium tin oxide, tin oxide, and zinc oxide, are highly preferred in optical devices. Among these metal oxides, zinc oxide is preferred for photodetectors because of its stable crystal structure and large exciton binding energy of 60 meV. Researchers have conducted studies on photodetectors with porous silicon-zinc oxide heterojunction structures. The importance of the stable operation of devices has been emphasized. Therefore, in this study, a porous silicon-based zinc oxide heterojunction structure suitable for photodetector production was formed, and the effect of aging on zinc oxide was investigated over time. As a result of the investigation, it was observed that the intensity decreased approximately 2.5 times at the end of 365 days owing to the aging of zinc oxide. In addition, UV spectroscopy measurements were performed to investigate the optical properties that affect their operation as photodetectors. Because the PS-ZnO heterojunction functions as a detector in the UV region, the absorption and reflectivity of the PS-ZnO heterojunction were investigated, especially in the UV region. From the measurements, it was observed that aging decreased absorption and increased reflectance. These findings underscore the negative impact of aging on photodetector performance.

Keywords: Porous silicon, Zinc oxide, Photodetector, Aging

1. Introduction

Silicon plays a central role in integrated circuit technologies and informatics, and serves as a primary material extensively employed for the production of various devices. These devices range from complex integrated circuits to economical solar cells. Silicon forms the basis of integrated circuits found in electronic devices. As complementary metal-oxide semiconductor (CMOS) production lines enable large-scale manufacturing, silicon-on-insulator (SOI) technology has emerged as a crucial platform for integrated photonics (Bloem, 1979; Mayer, 1984; Sieval et al, 2000; Guo et al, 2002; Shuchen et al, 2008; Cui et al, 2009; Westerveld, 2012; Garvey et al, 2020; De Matteis et al, 2020).

Silicon has a wide range of applications in integrated technology. They are utilized in the fabrication of thin-film transistors (TFTs), solar photovoltaic (PV) cells, peripheral circuits of liquid crystal displays (LCDs), and electrodes in Si integrated circuits (Periasamy et al, 2017). In contemporary settings, silicon plays a crucial role in various device applications and remains an integral component of the silicon integrated circuit technology (Lioudakis et al, 2008).

Photonics based on silicon and silicon nitride (Si₃N₄) are now employed for sensing assignments, encompassing tasks ranging from refractive index measurements to spectroscopic sensing (Subramanian et al, 2015). Silicon-on-insulator-based devices continue to be utilized in niche market applications, including high-temperature and radiation-hard integrated circuits (Colinge, 1998; Won et al, 2007; Zhong et al, 2011).

Silicon has been extensively incorporated into Application-Specific Integrated Circuit (ASIC) technology, particularly in designing readout electronics for silicon sensors in particle physics experiments (Won et al, 2007). The use of silicon-integrated circuits and micromachining technology enables the creation of microelectrode arrays and intricate electrical systems. There are several reasons for using silicon as a substrate in integrated technology. Silicon is a well-known and mature technology that is widely used in industry, making it a cost-effective option (Yusof et al, 2012). Second, silicon has a low thermal expansion coefficient, which makes it a suitable substrate for high-temperature applications (Gomes et al, 2011). Third, silicon has a high level of compatibility with other materials, such as III-V materials, making it a suitable substrate for hybrid integration (Gomes et al, 2011). Fourth, silicon-on-
Zinc oxide (ZnO) has various properties that make it useful in a wide range of applications. It has antimicrobial, anti-inflammatory, wound healing, catalytic, magnetic, optical, and electronic properties (Kaningini et al., 2022). ZnO is also used in piezoelectric gadgets, semiconductors, sensors, and for antimicrobial functions (Wasim et al., 2020). It has extraordinary physical and chemical properties that make it an important material for electrical, optical, mechanical, and scientific research. ZnO thin films have emerged as new and interesting materials owing to their electrical, optical, and piezoelectric properties (Rodriguez-Báez et al., 2007). Owing to their remarkable characteristics and unique physical and chemical properties, including remarkable chemical stability, anti-corrosiveness, low electron conductivity, broad radiation absorption, high photostability, and tremendous heat resistance, ZnO and metal-doped oxides are widely employed in the Nano World. (Mishra et al., 2022).

ZnO has good optical properties with respect to UV absorption (Weichelt et al., 2010; Zuo and Erbe, 2010). ZnO exhibits an optical transmittance of more than 70% in the visible region. The optical band gap of ZnO is around 3.7 eV (Czekalla et al., 2010). The optical properties of ZnO nanoparticles have also been studied, and they were found to exhibit nonlinear optical properties. The structural, morphological, and optical features of the ZnO nanoparticles were determined using X-ray diffraction, scanning electron microscopy, and ultraviolet-visible spectroscopy.

Properties of ZnO UV photodetectors include: - Wide bandgap of approximately 3.37 eV [34] - High radiation endurability (Tian et al., 2014) - Low visible absorption (Guo et al., 2023) - High transmittance in the ultraviolet (UV) region (Guo et al., 2023) - Excellent environmental stability (Guo et al., 2023) - Excellent photoresponse in the UV regime (Gebrehiwot, 2017) - Can be synthesized using a room ambient sonochemical process (Nayak et al., 2012) - Can be synthesized using a UV-assisted photocatalytic synthesis method (Chen et al., 2018) - Can be synthesized as a composite with reduced graphene oxide (rGO) (Chen et al., 2018; An et al., 2018) - Can be synthesized as a composite with single-walled carbon nanotube (SWNT) thin films (Ates et al., 2012) - Can be synthesized as a composite with zinc gallium oxide (ZnGa2O4) for deep-ultraviolet (DUV) photodetectors (Gebrehiwot, 2017) - Can be used to construct flexible and wearable photodetectors (An et al., 2018) - Can be integrated with other materials, such as lead sulfide (PbS) quantum dots, to induce a photocative conductivity (Dong et al., 2014) - Can be used in outdoor applications, such as wood coatings (Boruah et al., 2015) - ZnO nanowires (ZNWs) have a weak photon absorption and high recombination rate of electron-hole pairs, which limits their application in UV photodetection (Chen et al., 2018). However, this limitation can be overcome by using ZnO in composites with other substances, such as graphene (Yedurkar et al., 2016).

ZnO finds a wide range of applications across various fields. In electronics, it is used in piezoelectric devices, UV absorbers, and sensors. Additionally, it plays a role in communication, solar panel devices, and environmental protection. In the medical industry, ZnO is employed in drug delivery, nanomedicine, and gene delivery. Notably, ZnO nanoparticles show promise in biological sensing, biological labeling, and as antibacterial agents. In cosmetics, ZnO is utilized in sunscreens, whereas it serves as a food additive in the food industry. ZnO also contributes to biosensors, material sciences, and environmental remediation.

The synthesis of ZnO employs various methods, including chemical approaches, such as the sol-gel method, solvothermal and hydrothermal methods, and emulsion and microemulsion environment methods. Despite their potential applications, a significant hurdle in the development and utilization of ZnO-based materials for electrical and photonic purposes is the complexity of the carrier doping. The introduction of extra zinc or doping ZnO with elements like Al, Ga, or In simplifies the creation of ZnO (Pitiriscu et al., 2006; Amara et al., 2014; Mohsenzadeh and Moosavian, 2017; Nazir et al., 2018; Chikkanna et al., 2019; Dhevivamalar and Banu, 2019; Khan et al., 2021).

Aging in ZnO thin films refers to the changes occurring in the properties of the films over time due to exposure to environmental factors such as humidity and temperature (Yaklin et al., 2010). This process can lead to the formation of surface films primarily composed of hydrated tin and zinc oxy-hydroxide (Hanawa et al., 1987). The key characteristics of ZnO thin films include low electrical resistivity, excellent thermal stability, high optical transparency in the visible spectrum, and nontoxicity (Devasia et al., 2021; Amudhavalli et al., 2023). Defect sites in the microstructure, such as oxygen vacancies or zinc interstitials, play a crucial role in controlling the charge carrier mobility in thin-film transistor devices (Matysiak et al., 2018; Hoffman et al., 2021). Prolonged soft annealing times can induce an increase in the oxygen vacancy concentration in zinc tin oxide thin-film transistors. Additionally, when heated to 350 °C, the electrical conductivity of ZnO thin films doped
with aluminum deteriorates rapidly and unevenly. ZnO thin films are renowned for their advantageous characteristics, including low electrical resistivity, excellent thermal stability, great optical transparency in the visible spectrum, and non-toxicity (Konstantinidis et al., 2007; Huang et al., 2011; Nayak et al., 2013; Widyastuti, et al., 2022). According to the available literature, there is no specific information on the causes of aging in ZnO UV photodetectors. However, some studies have mentioned that the high radiation endurance and low visible absorption of ZnO make it a promising material for UV photodetector applications. Moreover, some commercial UV photodetectors made of silicon or gallium arsenide semiconductors require a filter to block visible and infrared light, and they may also be harmed by strong UV light because of aging faults that are created. (Sirkeli et al., 2018). Therefore, it can be inferred that aging of ZnO UV photodetectors may be related to the intensity and duration of UV radiation exposure. However, further research is required to determine the specific causes of aging in ZnO UV photodetectors.

There are several advantages and disadvantages to aging ZnO thin films. They are also non-toxic, inexpensive, and abundant in materials (Sellers et al., 2000). In addition, thin films of ZnO exhibit piezoelectric capabilities (Kuo et al., 2009). Thus, the use of ZnO thin films is growing in fields such as photovoltaic cells, photocatalytic materials, and poisonous gas sensors (Konstantinidis et al., 2007). However, there are also some disadvantages to aging ZnO thin films. For example, the concentration of mercury in a thin surface film is depleted after aging (Amudhavalli et al., 2023). Overall, the advantages and disadvantages of aging in ZnO thin films depend on their specific applications and desired properties.

There is limited information on how the aging of ZnO thin films affects UV photodetector performance. However, several studies have investigated the performance of ZnO thin film-based UV photodetectors. For example, one study reported the use of solution-based synthesis to create transparent and flexible ZnO nanowire UV photodetectors (Chen et al., 2018). Another study reported the performance enhancement of ZnO UV photodetectors using surface plasmons (Gebrehiwot, 2017). Additionally, UV photodetectors using thin sheets of indium ZnO with a binary cation exhibited a significant improvement in performance over their single-cation equivalents (He et al., 2022). Other studies have investigated the use of amorphous indium gallium ZnO film transistors for UV photodetector applications (Chang et al., 2012), p-n junctions of NiO thin films for UV photodiode characteristics, and the effect of the oxygen vacancy ratio on Ga2ZTO solar-blind photodetectors. Furthermore, the thermal stability of the aluminum-doped ZnO thin films was found to be significantly improved when exposed to UV ozone for a short time before heating. The oxygen plasma surface activation of electron-depleted ZnO nanoparticle films was also found to enhance the performance of the UV photodetectors. Finally, slightly doped ZnO films with manganese were found to exhibit increased photocatalytic performance compared to pure ZnO semiconductor thin films. Overall, although there is limited information on how aging specifically affects UV photodetector performance, several studies have investigated the performance of UV photodetectors based on ZnO thin films (Habibi and Aslari, 2011; Tyagi et al., 2012; Liu et al., 2017; Syu et al., 2018).

These studies provide information on various aspects of ZnO thin films, but only one study (Yaklin et al., 2010) has specifically noted accelerated aging studies. A prior study (Yaklin et al., 2010) investigated the effects of humidity and temperature on the performance of transparent conducting ZnO and included accelerated aging studies to determine the reliability factors and kinetic parameters.

ZnO thin films have been extensively studied because of their advantageous characteristics, which include their lack of toxicity, low electrical resistivity, high thermal stability, and high optical transparency. However, aging of ZnO thin films has been a topic of interest in recent studies. Yaklin et al. (2010) observed the electrical characteristics of conducting ZnO using an in situ electroanalytical technique under controlled air conditions, and discovered that one of the main causes of cell/module failure is water seeping into the modules in the field. Amudhavalli et al. (2023) studied the conduction mechanism of ZnO nanoparticles deposited using a low-cost nebulizer spray method. Kim et al. (2009) examined the optical and electrical properties of amorphous hafnium-indium-ZnO semiconductor thin-film transistors for thin-film transistor applications. Kappertz et al. (2002) investigated the correlation between the structure, stress, and deposition parameters of direct-current sputtered ZnO films. Indluru and Alford (2009) investigated how the thickness of Ag affects the optical and electrical characteristics of indium tin oxide–Ag-indium tin oxide multilayers. Park et al. (2021) investigated the antimicrobial effect of ZnO thin films formed by atomic layer deposition and evaluated their applicability to membrane surfaces. Konstantinidis et al. (2007) studied the deposition of ZnO layers using high-power impulse magnetron sputtering. Overall, the literature suggests that aging of ZnO thin films can affect their electrical, optical, and structural properties, and further research is needed to fully understand the aging mechanisms and develop strategies to mitigate their effects.

The integration of ZnO thin film-silicon heterojunctions has been a topic of interest in recent years owing to its potential applications in various electronic devices. A heterojunction is formed by combining two different materials with different electronic properties, which can lead to unique electronic properties at the interface. In this essay, we discuss the development of ZnO thin film-silicon heterojunctions and their potential applications.
One approach to forming a ZnO thin film-silicon heterojunction is by depositing indium tin oxide (ITO) and indium zinc oxide (IZO) thin films on vertically aligned silicon nanowire (SiNW) arrays (Chang et al., 2016). Another method involves depositing IZO thin film on a p-type porous silicon (PS) substrate to obtain an n-IZO/PS/p-Si heterojunction diode (Belaid et al., 2015). To create a heterojunction interface structure, reactively sputtered transparent and conductive Al-doped ZnO (AZO) films can be deposited on a macroporous silicon (MPS) substrate (Mendoza-Aguero et al., 2015). These methods demonstrate the potential of ZnO thin films in combination with silicon to create heterojunctions with unique electronic properties. ZnO thin film-silicon heterojunctions have potential applications in various electronic devices. For example, in photovoltaics, if titanium oxide is produced using a metal-organic chemical vapor deposition technique at substrate temperatures of only 80–100°C, a wide-bandgap heterojunction between crystalline silicon and titanium oxide can be employed (Avasthi et al., 2013). ZnO thin film-silicon heterojunctions can also be used in the production of thin metal oxide films by spray pyrolysis using supercritical CO$_2$-assisted nebulization of aqueous solutions (Sellers et al., 2000). In conclusion, the integration of ZnO thin film-silicon heterojunctions has shown potential for unique electronic properties and applications in various electronic devices. These heterojunctions have been developed through various methods, including depositing ITO and IZO thin films on vertically aligned SiNW arrays, depositing IZO thin films on p-type PS substrates, and reactively sputtering AZO films onto MPS substrates. The potential applications of ZnO thin film-silicon heterojunctions include tuning the accumulated electron concentration in TFTs, photovoltaics, and the production of thin metal oxide films. Further research is required to explore the full potential of ZnO thin film-silicon heterojunctions in electronic devices.

Competing evidence for an integrated technology composed of ZnO thin films and silicon heterojunctions has been found in various studies. For instance, Schlupp et al. (2013) suggested that, unlike the well-studied indium gallium ZnO, zinc-tin oxide is a promising n-type channel material for thin-film transistors and is composed solely of many components. Similarly, Masaud et al. (2011) proposed that materials suitable for the silicon process, such as thin-film ZnO, are still largely unexplored despite their potential to enhance the functioning of integrated silicon photonic devices. In addition, Ciolan and Motrescu (2022) claimed that as a first step toward creating an n-ZnO/p-Si heterojunction, ZnO thin films were produced at a comparatively low deposition temperature using pulsed laser ablation, a straightforward and non-toxic technique. Furthermore, Lee et al. (2016) suggested that because of its high mobility value, zinc oxynitride, a mixture of ZnO and zinc nitride, has been acknowledged as a potent replacement for traditional semiconductor films such as silicon and indium gallium ZnO. Finally, Bhoolokam et al. (2015) suggests that amorphous indium–gallium–ZnO thin-film transistors (a-IGZO TFTs) can be viewed as a replacement for amorphous silicon and low-temperature polycrystalline silicon in high-resolution liquid crystal displays for mobile applications and in organic light-emitting diode TVs in the display industry.

### 2. Materials and Methods

#### 2.1. Formation of Porous Silicon

Boron-doped p-type silicon with a resistivity of 0.001–0.005 Ωcm and thickness of 200 µm was preferred as a silicon wafer. Electrochemical anodic etching was performed using a double-tank Teflon cell to create pores in silicon (Gör and Karacalı, 2017). The solution was prepared as (1:2 (v/v) HF (40%) / EtOH (99%)) because the most controlled and smooth pore formation was observed in this ratio (Karacalı, 2003). In the electrochemical anodization method, a current density of 10 mA/cm$^2$ was applied to the silicon for 5 min. The structure proposed in this study is suitable for use in photodetectors. For this reason, a 650 nm PS layer was formed to reduce the recombination risk of the electron–hole pair. A scanning electron microscopy (SEM) image of porous silicon is shown in Figure 1.

**Figure 1.** SEM image of the pores obtained by applying 10 mA/cm$^2$ current density for 5 min.

#### 2.2. Synthesis of ZnO

During the preparation of the ZnO solution, zinc acetate dihydrate [Zn(CH$_3$COO)$_2$·2H$_2$O] was used as the starting material. In addition, monooethanolamine (C$_2$H$_7$NO, MEA) and 2-methoxyethanol (C$_3$H$_7$O$_2$) were used as the stabilizer and solvent, respectively. The solution was stirred at 60 °C for 2 hours to obtain a homogeneous and clear solution (Keskenler et al., 2017).

#### 2.3. The Deposition of ZnO Thin Film

ZnO thin films were produced on the PS using the spin coater technique. For this process, the PS to be used as a substrate was first placed in a rotary coating device (Laurell WS-650MZ-23NPPB) and the prepared ZnO solution was applied to the surface. The sample was then rotated at 3000 rpm for 25 seconds and the coating was...
applied. The coated film was sintered at 250 °C for 10 minutes to evaporate the solvent. This process was repeated nine times. Finally, the sample was annealed in air at 500 °C for 30 minutes (Keskenler et al., 2017).

3. Results and Discussion
3.1. Thin Film Characterization
As a result of this process, we observed the production of 130 nm thick ZnO thin films through the SEM images presented in Figure 2(a). Additionally, we performed energy-dispersive spectroscopy (EDS) using a Quanta FEG 250 and X-ray diffraction (XRD) measurements for characterization after producing the thin film on PS. It was confirmed that the ZnO thin film was successfully coated onto the silicon. The EDS and SEM results are shown in Figure 2(b), and Figure 3, respectively.

The SEM image of the ZnO thin film heterostructure on PS is shown in Figure 2. a. When the porous layer thickness was ~650 nm, the thickness of the ZnO thin film was measured to be ~136 nm. Figure 2.b shows the EDS results of the ZnO thin-film heterostructure on the PS. In the EDS results, in addition to the Zn and O peaks of ZnO, peaks of B-doped Si were also observed. As shown in Figure 3, several characteristic peaks can be observed in the XRD spectrum of ZnO. The most prominent peak is typically located at approximately 2θ = 34.4°, corresponding to the (002) crystal plane of the hexagonal wurtzite ZnO. Other peaks can be observed at different 2θ angles, representing different crystal planes and orientations of ZnO. By analyzing the positions, intensities, and shapes of these peaks, valuable information regarding the crystal structure, phase purity, and crystallinity of the ZnO sample can be obtained.

When comparing the results obtained in Figure 3 with the data from the literature presented in Figure 4, the dominant peak observed is identified as (002), and it is evident that the ZnO peaks are aligned. In Figure 4, the XRD results of thin films produced with 0.5, 1 and 1.5 M ZnO solutions prepared in the study conducted by (Keskenler et al., 2017) are presented. The ZnO thin film prepared on PS was stored in a climate room where special conditions were provided in a dark environment at 23.4 °C and 55% humidity for one year. The ambient conditions, including humidity and temperature, are shown in Figure 5.

The XRD measurement results of the sample kept in a dark environment at 23.4 °C and 55% humidity for 365 days are shown in Figure 6. As shown in Figure 6, the dominant peak is (002), and it is observed that the ZnO peaks match. However, according to the measurement results shown in Figure 3, the intensity decreased considerably. While the ZnO peak is dominant in the unaged sample shown in Figure 3, it is weakened in the aged sample, as shown in Figure 6. Therefore, while the ZnO peak is dominant in the unaged sample, the Si peak is more dominant in the aged sample.

Figure 2. EDS and SEM results of ZnO thin film on PS.

Figure 3. XRD results of ZnO thin film on PS.
Figure 4. XRD result of ZnO thin film coating taken from the literature.

Figure 5. Device showing the ambient conditions under which the PS-ZnO heterostructure is left to age.

Figure 6. XRD results of PS-ZnO heterojunction kept in dark environment at 23.4 °C and 55% humidity for 1 year.

Figure 7 illustrates the absorption and reflectance graphs of a 1-year aged and unaged PS-ZnO heterojunction, measured using a Shimadzu UV-3600 Plus UV-VIS-NIR Spectroscopy device. In Figure 7(a), the absorption percentage (~12%) of the unaged sample is higher than the absorption percentage (~8%) of the 1-year aged sample, whereas the reflectivity shows the opposite trend. The reflection percentage (~4%) of the unaged sample is smaller than that (~6%) of the 1-year aged sample, as shown in Figure 7(b). For optimal photodetector performance, high absorption and low reflectivity are desirable. Efficient operation relies on capturing light at a high rate, while minimizing the rate of reflection. As shown in Figure 7, aging adversely affects the optical performance of the photodetector. Given that PS-ZnO heterojunction photodetectors operate in the UV region, particular attention was paid to investigating the UV region.

Figure 7. Absorption and reflectance graphs of PS-ZnO heterojunction (a) unaged PS-ZnO heterojunction (b) aged for 1 year at 23.4 °C and 55% humidity in the dark.

4. Conclusion
While the ZnO peaks dominate in Figure 3, it is evident that the PS peak becomes more prominent, as shown in Figure 6. This indicates a transition in the crystal structures of the films from a single to polycrystalline nature over time (Keskenler et al., 2017). In other words, time-dependent depressions and agglomerations manifest in the structure, leading to a decrease in the intensity over time (Wojtasik et al., 2023). This results in...
deterioration of the homogeneity within the structure. For semiconductor devices, maintaining homogeneity is crucial for a stable operation. As shown in Figure 7, UV measurements were conducted to investigate the effect of aging on the optical properties of the photodetector in the PS-ZnO heterojunction. The measurements revealed that aging decreased the optical performance of the photodetector.

Considering these observations, studies focusing on delaying aging, which is a critical factor in determining the working life of devices, hold promise.

**Author Contributions**
The percentage of the author(s) contributions is presented below. All authors reviewed and approved the final version of the manuscript.

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C= Concept, D= design, S= supervision, DCP= data collection and/or processing, DAI= data analysis and/or interpretation, L= literature search, W= writing, CR= critical review, SR= submission and revision, PM= project management, FA= funding acquisition.

**Conflict of Interest**
The authors declared that there is no conflict of interest.

**Ethical Consideration**
Ethics committee approval was not required for this study because there was no study on animals or humans.

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