

## **Cubic Silicon Carbide as Photoelectrode for Hydrogen Generation from Solar-driven Water Splitting**

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### **PURPOSE AND AIMS**

This project opens up a new research field of photoelectrochemical (PEC) water splitting into hydrogen using solar energy based on cubic silicon carbide (3C-SiC) electrode. It aims at exploring 3C-SiC toward the generation of solar hydrogen, which is regarded as a renewable, sustainable, environment-friendly energy source.

Photoelectrochemical water-splitting devices, which convert solar energy and water into H<sub>2</sub> and O<sub>2</sub>, attract a great interest due to its potential to use the abundance of solar energy and water on Earth. Hydrogen is an attractive energy carrier, advantages being its high energy density (three times that of gasoline) and clean by-product (water) when combusted for energy generation. Thus, harvesting solar energy to produce hydrogen can support reducing the problems of the depletion of fossil fuels, the emissions of CO<sub>2</sub>, the environmental pollution, and the energy security of our society. However, it is an enormous challenge to find an efficient visible light-absorption semiconductor electrode which has suitable semiconductor-redox energetics for water splitting. Among all commonly used materials, 3C-SiC has outstanding properties to convert visible sunlight energy and water into hydrogen, but 3C-SiC has not been available in high quality. Recently, we have demonstrated that state of the art quality of 3C-SiC can be grown by a sublimation epitaxial method [1-2]. We will combine existing expertise in crystal growth, innovative concepts and intensive international collaborations in order to explore 3C-SiC for the solar hydrogen application.

In this project, 3C-SiC will be tailored as a photoelectrode to absorb and convert solar energy into hydrogen via a photoelectrochemical water-splitting cell. In order to realize a high solar-to-hydrogen conversion efficiency using 3C-SiC, we will

- Adapt a growth process of high-quality 3C-SiC to produce free standing layers;
- Explore suitable doping concentrations for both n- and p-type 3C-SiC which give rise to the optimum solar-to-hydrogen conversion efficiency;
- Establish a detailed knowledge on the influence of the carrier lifetimes, transport properties, doping concentrations on the hydrogen conversion efficiency;
- Implement the best metal candidates to match n- and p-type 3C-SiC electrodes together with the potential photo-corrosion effect on the 3C-SiC in different PH electrolytes;
- Open up a new approach of improving the solar-to-hydrogen conversion efficiency by means of the nanostructured n- and p-type 3C-SiC electrodes which previously never have been studied;
- Demonstrate a practical 3C-SiC PEC cell prototype for hydrogen generation with significantly improved efficiency.

In this project we combine expertise in crystal growth, semiconductor physics and surface chemistry for development of advanced PEC cell which could pave the way for ground-breaking technologies for energy and environmental applications. Moreover, we establish a multidisciplinary and international collaboration to expand the 3C-SiC toward the solar hydrogen application. In particular, we will have exchange with research groups in Meijo University (MU), Nagoya Institute of Technology (NIT), Vilnius University (VU) and Denmark Technical University (DTU).

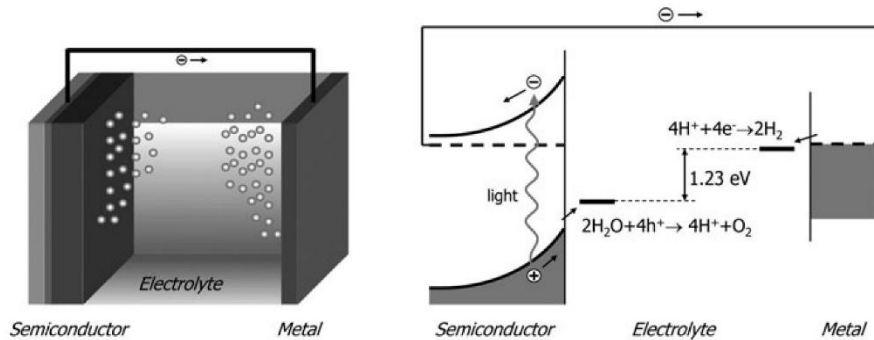
At IFM, Linköping University (LiU) there is a strong competence within the fields of SiC growth and characterizations. This is supported by an infrastructure regarding equipment and resources dedicated to wide band gap semiconductors that are unique in the research community. In this project, we open a new approach for 3C-SiC as water splitting material.

## 1. INTRODUCTION

Nowadays, due to the depletion of the conventional fossil energy and ever more evident environmental impact of air pollutants and greenhouse gas, CO<sub>2</sub>, mainly produced by the combustion of fossil fuels, it is becoming crucial to search for renewable energy sources. Solar energy is the most abundant, inexhaustible and clean energy source. With  $3 \times 10^{24}$  joules a year striking the surface of the earth, the solar energy is about 10,000 times more than the current energy consumption by global population. This means that our energy needs would be satisfied by covering 0.1% of the Earth's surface with solar cells which have an efficiency of 10% [3]. However, it is still an enormous challenge to capture, convert and store the Sun energy. The photovoltaic cell, the most common device to collect solar energy, only generates electricity during day time. Hence, energy must be used immediately or stored in a secondary device such as a battery.

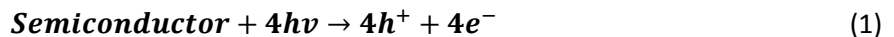
Direct conversion of solar energy into hydrogen from water splitting provides another attractive, clean and sustainable way to harvest solar power. Hydrogen has a high energy density (120 J/g, about three times that of gasoline) and has a clean by-product (water) when combusted for energy generation. Hydrogen is also a highly versatile fuel. It can be efficiently converted into electricity using a fuel cell or directly drive an internal combustion engine.

The photoelectrochemical water splitting into H<sub>2</sub> and O<sub>2</sub> by semiconductors has attracted much attention because of its potential to use the abundance of solar energy and water on Earth. The principle of PEC hydrogen generation is relatively simple. As seen in Fig. 1, the typical PEC water splitting cell is composed of a semiconductor photoelectrode and a metal counter electrode which are immersed in the aqueous electrolyte [4]. The semiconductor photo-electrode absorbs the sunlight energy and converts incident photons to electron-hole pairs. These carriers are spatially separated from each other by the presence of a built-in electric field which is formed due to the surface potential. The photo-generated minority carriers are swept toward the n-type semiconductor/electrolyte interface to oxidize water (O<sub>2</sub> generation). The photo-generated majority carriers are transported to the metal electrode to reduce water (H<sub>2</sub> generation). For p-type case, H<sub>2</sub> is generated on the semiconductor surface and O<sub>2</sub> on the metal surface. Therefore, H<sub>2</sub> and O<sub>2</sub> can be generated separately by the PEC water splitting only consuming the sunlight energy.



**Fig. 1** Illustration of a photoelectrochemical cell comprising a n-type semiconducting photoanode and a metal cathode. The principle of operation for H<sub>2</sub> generation is presented on the right side [4].

As seen in Fig. 1, sunlight generates electrons in the conduction band and holes in the valence band:



At the interface of the semiconductor and electrolyte, the photo-generated holes result in the splitting of water molecules into O<sub>2</sub> and hydrogen ions:



Simultaneously, the photo-generated electrons are transferred to the cathode, resulting in the reduction of hydrogen ions into H<sub>2</sub>:



Accordingly, the reactions (2)+(3) describe the overall PEC water-splitting process, which needs the energy of 237.2 kJ/mol (corresponding to 1.23 eV) for PEC water splitting.

## **2. SURVEY OF THE FIELD**

### **2.1 Semiconductor Criterions for PEC Water Splitting**

The key component of the PEC cell is the semiconductor photoelectrode, which should meet some specific requirements [4]:

- (i) Suitable bandgap for the efficient (visible) sunlight absorption;
- (ii) Suitable conduction band edge and valence band edge for straddling the reduction and oxidation potentials of water splitting;
- (iii) High chemical stability in the electrolyte with and without light illumination;
- (iv) Efficient charge transport in the semiconductor.

So far, it is still a big challenge to find a semiconductor suitable to work as an efficient photoelectrode although much research effort has been made since the pioneering work of A. Fujishima and K. Honda with using  $\text{TiO}_2$  in 1972 [5].  $\text{TiO}_2$  is one of the most extensively studied materials for the photoanode due to its higher chemical stability. However, the overall efficiency of using  $\text{TiO}_2$  as a solar photoanode is rather low due to the fast carrier recombination and its large band gap of 3.2 eV which only absorbs 4% (ultraviolet part) of the solar energy. Theoretical results indicate that bandgaps greater than 3.2 eV result in an upper limit of 1.23% on the hydrogen conversion efficiency [4,8].

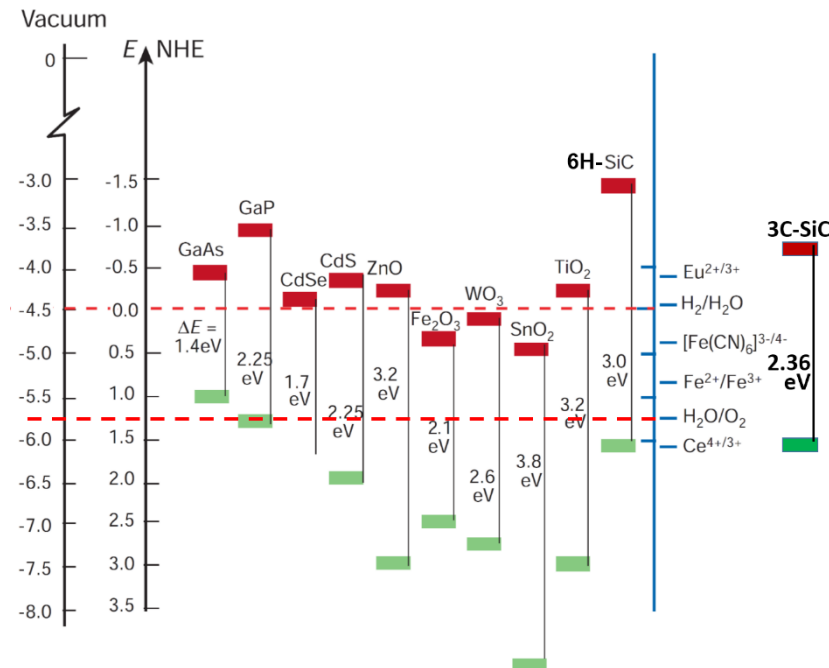
To fulfil the first requirement, the small bandgap semiconductor is needed for efficient visible light absorption. However, as a compromise, the minimum bandgap is determined by the energy required to split water (1.23 eV) plus the thermodynamic losses (0.3–0.4 eV) and the over potentials that are required at various points in the system to ensure sufficiently fast reaction kinetics (0.4–0.6 eV) [4]. This results in a need of the minimum bandgap of 1.9 eV, corresponding to an absorption onset at 650 nm. On the other hand, the intensity of sunlight drops dramatically below 400 nm, indicating an upper limit of 3.1 eV of the bandgap. Hence, the optimum value of the bandgap should locate somewhere between 1.9 and 3.1 eV within the visible range of the solar spectrum.

The second requirement, suitable band edges to straddle the reduction and oxidation potentials, is the principal parameter which determines the PEC water splitting ability of the semiconductor. Specifically, the valence band of the semiconductor must be more positive than the oxidation potential and the conduction band edge must be more negative than the reduction potential. In other words, the reduction and oxidation potentials of  $\text{H}_2/\text{H}_2\text{O}$  and  $\text{H}_2\text{O}/\text{O}_2$ , (two red dashed lines in Fig. 2) must be positioned within the bandgap of the semiconductor. Fig. 2 shows the band positions of several semiconductors in contact with aqueous electrolyte at pH=1, along with the reduction and oxidation potentials of water [3]. As seen, very few semiconductors fulfil this requirement. Among them,  $\text{TiO}_2$ , ZnO and 6H-SiC have too larger bandgap (>3 eV), which results in a rather low hydrogen conversion efficiency. Since most non-oxide semiconductors (for example, GaAs) have more negative conduction band edge than water reduction potential  $\text{H}_2/\text{H}_2\text{O}$ , they are able to reduce, but not oxidize water. In contrast, most oxide semiconductors ( $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$ ) are able to oxidize, but not reduce water. Hence, a PEC cell using these oxide materials require an external electrical bias for the water splitting.

The third requirement of high chemical stability against (photo-) corrosion is another severe parameter. A number of non-oxide semiconductors which exhibit suitable semiconducting properties for solar energy conversion (CdS, GaP, CdSe) are not stable in the water during the oxidation reaction because these materials either dissolve or form a thin oxide film which prevents electron transfer across the semiconductor/electrolyte interface.

The fourth requirement, the efficient charge transport, is also an important parameter to determine the overall solar-to-hydrogen efficiency. The photo-generated minority carries should have a long lifetime/long diffusion length to reach the semiconductor/electrolyte interface before

recombination. The carrier lifetime,  $\tau_R$ , are related to the minority carrier diffusion,  $L_D$ , through  $L_D = \sqrt{D\tau_R}$ , where the diffusion coefficient,  $D$ , is related to the carrier mobility,  $\mu$ , by the equation  $D = kT\mu/e$ . Some oxide materials ( $\text{TiO}_2$ ,  $\text{WO}_3$ ) fulfill this requirement, however, it is one of the main drawback to cause a poor conversion efficiency for some materials such as  $\text{Fe}_2\text{O}_3$  [4]. Most metal oxides usually has high electron mobility but a low hole mobility.



**Fig. 2** Band positions of several semiconductors in contact with aqueous electrolyte at pH 1 relative to the reduction and oxidation potentials of  $\text{H}_2/\text{H}_2\text{O}$  and  $\text{H}_2\text{O}/\text{O}_2$  (two red dash lines) [3]. On the right side the band position of 3C-SiC are also presented. It should be noted that the small bandgap of 2.36 eV and the fact that the conduction band edge is more negative than the reduction potential and the valence band edge is more positive than the oxidation potential, enable 3C-SiC to absorb visible sunlight and split water in PEC cell spontaneously.

## 2.2 Limits of the commonly used semiconductors for PEC water splitting

The commonly studied semiconductor for PEC water splitting are the oxides such as  $\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and III-V materials. As mentioned above, the oxides are stable in aqueous solution but their band gaps are either too large for efficient light absorption or their semiconductor energetic characteristics are too poor for water splitting. Many III-V semiconductors which exhibits the suitable properties for solar energy conversion ( $\text{CdS}$ ,  $\text{GaP}$ ) suffer from the photo-corrosion. Indeed, a monolithic tandem cell based on a p-type  $\text{GaInP}_2$  photo-cathode biased by a  $\text{GaAs}$  p-n junction solar cell demonstrated a high hydrogen conversion efficiency of 12.4% under an illumination intensity of 11 suns [6]. Such a tandem configuration suffers from the drawbacks such as too high cost and the requirement of an external bias. However, the main problem is the severe photo-corrosion of semiconductors, which results in the very short lifetime (in hours instead of years).

Recently,  $\text{Fe}_2\text{O}_3$  attracts much interest due to its favorable bandgap of 2.1 eV and chemical stability. However,  $\text{Fe}_2\text{O}_3$  has some drawbacks toward PEC reaction [7]: First, the conduction band edge is much lower than the water reduction potential. Thus, it requires an external voltage to carry out water reduction. Second,  $\text{Fe}_2\text{O}_3$  has a very small hole diffusion length (2-4 nm), which results in the low probability for holes to participate in water oxidation.

## 2.3 3C-SiC for PEC water splitting

3C-SiC has outstanding properties such as excellent mechanical strength, chemical inertness and high saturated drift velocity, and high electron mobility. Most importantly, 3C-SiC is almost a perfect material to meet all criteria for PEC water splitting stated above:

- First, 3C-SiC has an indirect bandgap of 2.36 eV at room temperature, which is larger than the minimum energy value of 1.9 eV required to split water and also satisfies the first requirement to absorb the visible sunlight. Theoretically, Murphy et al. predicted a maximum efficiency of

# APPENDIX A – RESEARCH PROGRAMME

## CUBIC SILICON CARBIDE AS PHOTOELECTRODE FOR HYDROGEN GENERATION FROM SOLAR-DRIVEN WATER SPLITTING

16.8% for a hypothetically ideal material with an optimum bandgap of 2.03 eV [8]. Fortunately, the bandgap of 3C-SiC is much close to this optimum value. Therefore, in principle, a very high solar-to-hydrogen efficiency (close to the theoretical maximum efficiency) can be obtained in the 3C-SiC PEC cell.

- Second, in contrast to  $\text{Fe}_2\text{O}_3$ , 3C-SiC elegantly fulfills the requirement to straddle the reduction and oxidation potentials of water splitting, seen in Fig. 2, the conduction band edge of 3C-SiC locates above the reduction potential of  $\text{H}_2/\text{H}_2\text{O}$  while the valence band edge is positioned below the oxidation potential of  $\text{H}_2\text{O}/\text{O}_2$ . This results in the spontaneous (without any external electric bias) water splitting at 3C-SiC photo-electrode. Indeed, in March 2014, Kato et al. demonstrated this phenomenon [9].
- Third, it is relatively easier to grown p-type 3C-SiC, which acts as photocathode to form  $\text{H}_2$ , consequently offers some protection against photo-corrosion.
- 3C-SiC also satisfies the fourth requirement (efficient charge transport) because of its high electron mobility of  $1000 \text{ cm}^2/\text{Vs}$  and hole mobility of  $320 \text{ cm}^2/\text{Vs}$ . A high mobility is especially desirable in photoelectrodes with an indirect bandgap, because these materials require a large thickness to absorb all the incident light, which means that photo-generated electrons and holes have to travel large distances before reaching the interface. As seen in Table 1, 3C-SiC has much higher carrier mobilities than most of common semiconductors for PEC water splitting. Moreover, as shown below in the part of preliminary results, we have grown a high quality 3C-SiC with the measured minority carrier lifetime of  $8.2 \mu\text{s}$ , which corresponds to a large diffusion length  $D$  of  $\sim 50 \mu\text{m}$ . This is also much larger than most commonly studied semiconductor photoelectrodes and thus contributes to a high minority transport efficiency to interface for water splitting.

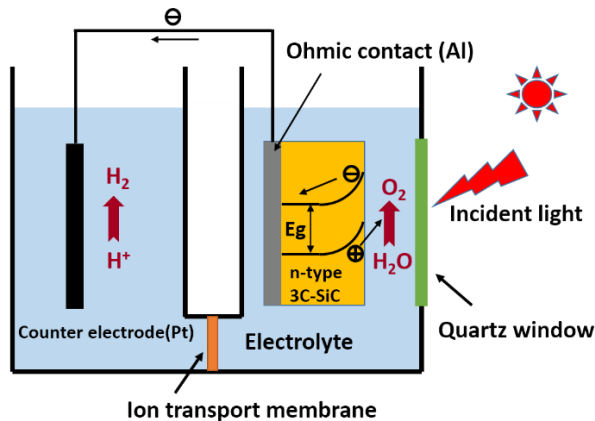
**Table 1** Carrier mobilities for some commonly used photoelectrode semiconductors at room temperature [4,10].

<sup>a</sup>Theoretical value, <sup>b</sup>@1200K, <sup>c</sup>@1400K

Material	3C-SiC	CdS	TiO <sub>2</sub>	WO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	p-Cu <sub>2</sub> O	p-CuAlO <sub>2</sub>	p-SrCu <sub>2</sub> O <sub>2</sub>	p-CuMnO <sub>2</sub>
Electron mobility ( $\text{cm}^2/\text{Vs}$ )	1000	340	NA	~10	<sup>b</sup> 0.1	NA	NA	NA	NA
Hole mobility ( $\text{cm}^2/\text{Vs}$ )	320	50	<sup>a</sup> $2 \times 10^{-3}$	NA	<sup>c</sup> 0.2	90	10	0.46	$3.5 \times 10^{-6}$

### 3. PROJECT DESCRIPTION

In this project, we explore 3C-SiC as a photo-electrode for  $\text{H}_2$  generation by PEC water splitting since it has very attractive properties. The schematic setup is shown in Fig. 3. By means of such a “U” shape cell and an ion transport membrane, we can generate and collect  $\text{O}_2$  on 3C-SiC and  $\text{H}_2$  on metal electrodes separately. If using p-type 3C-SiC, the principle of the operation is same as the n-type case but 3C-SiC will act as a photo-cathode to form  $\text{H}_2$  instead of  $\text{O}_2$ .



**Fig. 3.** Schematic diagram of proposed PEC cell setup composing of n-type 3C-SiC and metal cathode

**APPENDIX A – RESEARCH PROGRAMME**  
**CUBIC SILICON CARBIDE AS PHOTOELECTRODE FOR HYDROGEN GENERATION FROM SOLAR-DRIVEN WATER SPLITTING**

Research activities which will be performed in this project are divided into interconnected work-packages (WPs) which are distributed within 4 years project period. The schematic diagram of project implementation plan is demonstrated below.

	Year 1				Year 2				Year 3				Year 4				Partners involved
WPs	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	
WP1																	LiU
WP2																	LiU
WP3																	LiU, NIT
WP4																	LiU, NIT
WP5																	LiU, VU, MU
WP6																	LiU, DTU

### WP1 - Growth of high-quality free standing 3C-SiC

Although 3C-SiC has very promising properties for solar hydrogen application, it suffers from a defective quality issue for last decades. A major reason is its metastable phase formation, which makes it to form only at certain temperatures, and sensitivity to vapor phase composition. Recently, most 3C-SiC materials demonstrated for the PEC water splitting were grown on silicon substrates [11]. The large lattice (20%) and thermal (8%) mismatch using silicon substrates results in an inferior crystals with high densities of defects that hinders the implementation of its beneficial properties in the water splitting application.

Most recently, we have demonstrated that state of the art quality of 3C-SiC can be grown on low off-cut 6H-SiC substrate (lattice mismatch ~0.1%) [1-2]. We show the best photoluminescence and XRD results ever observed, in particular, a considerably long carrier lifetime of 8.2  $\mu$ s [1-2] in a 760  $\mu$ m thick bulk like 3C-SiC. To optimize the solar-to-hydrogen conversion efficiency, in this project we will explore the free standing 3C-SiC with different thicknesses that will be designed according to the net doping concentration, carrier lifetimes and light penetration depth.

The reason for using free-standing 3C-SiC is based on the following considerations: First, since 3C-SiC is an indirect bandgap material, a quite thick layer is required to absorb most of the incident visible light. Second, the 3C-SiC usually has a degradation layer (more defects such as dislocations and stacking faults) at the 3C-SiC/6H-SiC substrate interface. Thus, in this work-package, we will grow a very thick 3C-SiC and then polish away the substrate and a large part of 3C-SiC which contains this interfacial degradation layer in order to have a high quality free standing layer. All growth activities will be performed at Linköping University (LiU).

### WP2 - n-type and p-type doping control of 3C-SiC

In both the n- and p-type 3C-SiC photo-electrodes, the net doping concentration controls the photo-response current and also affects the carrier lifetimes. For the n-type case, nitrogen will be used as a donor dopant. For the p-type case, both aluminum and boron doping will be investigated. In this project, we will explore the optimum doping concentration for both the n-type and p-type 3C-SiC photoelectrodes. Hall-effect measurement will be employed to study the carrier transport properties. The experimental work will be compared with theoretical simulations of the dependency of doping concentrations, carrier mobility and minority carrier lifetime on the hydrogen conversion efficiency. The target is to explore an optimum condition for a high solar-to-hydrogen efficiency. The growth of doped 3C-SiC will be done at Linköping University (LiU).

### WP3 - Metal counter electrode materials

Due to very limited knowledge on PEC water splitting using 3C-SiC, it is still a new research field to explore which metal can be used as counter electrode to match 3C-SiC for an optimum hydrogen conversion efficiency. Thus, different counter electrode materials such as Pt, Ni, Cu, RuO<sub>2</sub> will be



studied for both n- and p-type 3C-SiC cases. *Research activities within this work-package will be performed in close collaboration with Nagoya Institute of Technology (NIT) in Japan.*

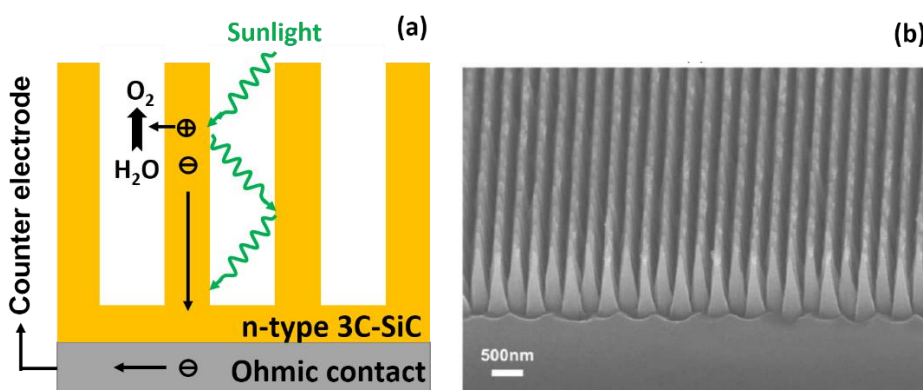
#### **WP4 - Photo-corrosion of n-type 3C-SiC versus p-type 3C-SiC**

In the case of using n-type 3C-SiC as a photoanode to create O<sub>2</sub>, it is not clear whether it suffers from an oxidation on the surface of 3C-SiC or not. So far, there is very limit knowledge on this field. We will perform a detailed study in this aspect. The time-dependent photo-current will be systematically studied together with the case of using the p-type 3C-SiC as photocathode. The detailed chemical reaction mechanism at the 3C-SiC/electrolyte interface will be investigated. *This will be done by the collaboration with the project partner Nagoya Institute of Technology (NIT) in Japan.*

#### **WP5 - Carrier lifetime in 3C-SiC**

The long carrier lifetime could increase the photo-current and thus improve the overall solar-to-hydrogen conversion efficiency. The space charge width,  $W$ , is mainly determined by the net doping concentration. The minority carrier diffusion length is related to the carrier lifetime through  $L_D = \sqrt{D\tau_R}$ . In the indirect bandgap material, most of the electron-hole pairs are generated far away from the surface, and the carriers recombine before reaching the interface. Only charge carriers generated within a distance  $L_D + W$  from the surface contribute to the photocurrent. Thus, the long minority carrier lifetime and high mobility are required to have a high conversion efficiency. In this project, we will perform a systematical study on the carrier lifetime by microwave photo-conductivity decay ( $\mu$ -PCD) measurements together with time-integrated and time-resolved photoluminescence characterizations. The limit of the carrier lifetime could be the crystallographic defects such as vacancies, interstitials, dislocations, stacking faults. By combining the  $\mu$ -PCD and Deep Level Transient Spectroscopy (DLTS) techniques, we will study the main defects which reduce the carrier lifetimes. Consequently, this will give a feedback to guide the growth or post-treatment for a reduction of such specific defects. *Theoretical predictions and experimental carrier lifetime measurements will be performed in combined efforts between Linköping University (LiU), Vilnius University (VU) and Meijo University (MU).*

#### **WP6 - Nanostructured 3C-SiC Electrodes**



**Fig. 4.** (a) Schematic 3C-SiC nanowire array photo-anode. (b) SEM image of the nanostructured pattern on SiC fabricated using the reactive-ion etching [12].

Nanostructured electrode morphologies can be used to improve the solar-to-hydrogen conversion efficiency. The first advantage is that a nanostructured morphology increases the surface area, and thus greatly enhances the overall charge transfer kinetics at the semiconductor/electrolyte interface. A second significant advantage is the shorter diffusion path lengths for the photo-generated minority carriers, seen Fig. 4 (a). In this project, we will employ the reactive-ion etching to fabricate nanostructured 3C-SiC electrodes. Recently, Y. Ou et al [12] demonstrated the feasibility to achieve a nanostructured pattern on our SiC layers, seen in Fig. 4(b). We will employ a similar dry etching method to make different patterns such as pyramids, or wires with different aspect ratios on 3C-SiC.

Apparently, the wire diameter should be designed according to the condition of the light penetration depth, doping concentration, and the diffusion length. Such simulations and experimental works, in particular, the fabrication of nanostructured 3C-SiC will be done together with researchers from Demark Technical University (DTU).

### **Project Timetable**

**Year 1: WP1, WP2 and WP3.** The main work will focus on the growth and n- and p-type doping of 3C-SiC. Different growth parameters will be explored to grow high-quality 3C-SiC free standing layers. Material characterizations such as XRD, low temperature photoluminescence (LTPL) will be done to give the feedback for the optimization of the growth conditions. Different metal electrodes will be assessed to match both the n- and p-type 3C-SiC.

**Year 2: WP2, WP3, WP4 and WP5.** The doping concentrations of n- and p-type 3C-SiC will be further optimized. Suitable metal electrode will be explored to for optimum hydrogen conversion efficiency. The solar-to-hydrogen conversion efficiency and photo-corrosion will be studied by using a series of n-type and p-type 3C-SiC electrodes in different PH electrolytes. Considering the effect of minority carrier lifetime, mobilities, donor and acceptor concentrations on the photocurrent, simulations and experimental works will be explored to improve the PEC cell performance.

**Year 3: WP4, WP5 and WP6.** In both n- and p-type 3C-SiC, correlation between the carrier lifetime and the crystallographic defects will be systematically studied by  $\mu$ -PCD and DLTS measurements. The target is to find out the main defects that reduce carrier lifetimes. This will give a feedback to guide the growth or post-treatment for a reduction of such specific defects. Nanostructured morphologies on 3C-SiC will be fabricated and photo-corrosion effect on their surface will be studied. Together with these studies, the details of the factors which limit the hydrogen generation efficiency will be explored.

**Year 4: WP5 and WP6.** The carrier lifetime in the nanostructured 3C-SiC will be studied by considering the surface recombination effect. Different patterns such as pyramids, or wires with different aspect ratios will be studied for an improvement of the  $H_2$  generation efficiency. Simulations and experimental work will be explored for the improvement of the  $H_2$  generation efficiency. A practical 3C-SiC PEC water splitting prototype for  $H_2$  generation will be demonstrated.

### **4. PRELIMINARY RESULTS**

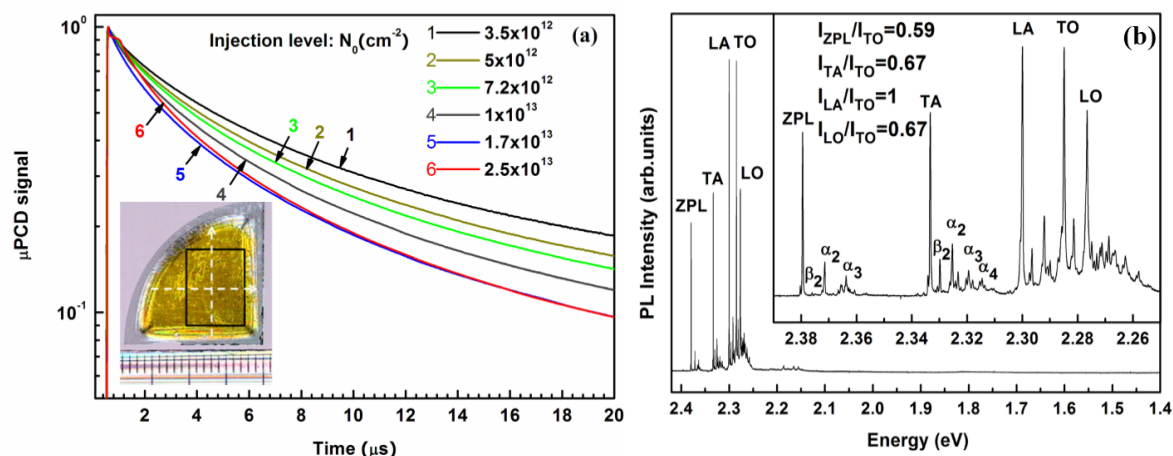
Despite the progress of different growth techniques in the last decade, free standing or thick ( $>100\ \mu\text{m}$ ) 3C-SiC layers grown on either undulant Si, or 4H-SiC, or 6H-SiC substrates usually show inferior crystalline quality. As a consequence, they show very short carrier lifetime, ranging from a few to 120 ns [13]. These values are at least one order of magnitude lower than the lifetime in the more mature 4H-SiC (few  $\mu\text{s}$ ) [14].

Most recently, we demonstrated that state of the art quality of 3C-SiC can be grown on low off-cut 6H-SiC substrate. We show the best photoluminescence and XRD results ever observed and a considerably long carrier lifetime of 8.2  $\mu\text{s}$  [1-2]. In fact, a comparison of experimental lifetimes with numerical simulations indicates that the real bulk lifetime in such high quality 3C-SiC is in the range of 10-15  $\mu\text{s}$  [1].

The XRD and LTPL show that 3C-SiC can indeed reach a very high crystal quality [1-2]. The average FWHM values of XRD omega rocking curve is approximately 91 arcsec [2], which is close to the values (9-70 arcsec) measured in commercial 4H-SiC. As seen in Fig. 5 (b), LTPL emission is only governed by the nitrogen-bound exciton zero-phonon line (ZPL) and its phonon replicas (TA, LA, TO and LO) without any defect-related emissions. Notably, the line width of the nitrogen-bound-exciton peak is rather narrow, around 0.2 meV (spectral resolution about 1 Å). Besides the nitrogen-bound-exciton peaks, many multiple bound exciton complex lines (denoted by  $\alpha_m$ , up to  $m=4$ ) are also well resolved. Additional fine lines ( $\beta_m$ ) due to excited electron states were also observed. Clearly, in



order to bind more than one exciton at a nitrogen donor, a longer carrier lifetime (high quality material) is required, otherwise the photo-generated carriers would quickly recombine before bounding more electron-hole pairs to the nitrogen donors ( $m=2,3,4\dots$ ). Thus these multiple bound excitons have been rarely observed in 3C-SiC and regarded as a characteristic of high-quality material. XRD and LTPL results demonstrate that the 3C-SiC indeed reach a high crystal quality, which explains the significantly improvement of the carrier lifetime.



**Fig.5**  $\mu$ -PCD curves (a) and LTPL spectrum (b) of the 3C-SiC shown in the inset. XRD  $\omega$ -rocking curve mapping measured on the solid square area indicated in the inset shows an average XRD FWHM value of 91 arcsec [1-2].

According to the criteria for PEC water splitting stated above, our high quality 3C-SiC with long minority carrier lifetime should ensure a high performance on the solar hydrogen application.

## 5 PERSONNEL INVOLVED IN THE PROJECT

The project leader, **Dr. Jianwu Sun**'s expertise is mainly in epitaxial growth of semiconductors (ZnO, GaN, SiC) and structural, optical, and electrical characterizations such as Raman, LTPL,  $\mu$ PCD, Hall-effect characterizations, and theoretical simulations. He got his PhD degree in 2008 and his PhD work was focusing on the MBE growth of p-type ZnO, quantum wells and LED applications. Starting from 2009, he has been working on the growth and characterizations of 3C-SiC in CNRS-Montpellier University 2 and continued the research on undoped 3C-SiC, 4H-SiC and 6H-SiC in Linköping University, Sweden.

Docent. Mikael Syväjärvi has initiated 3C-SiC growth for the photovoltaic application.

## 6 INTERNATIONAL COLLABORATION

The main applicant will have a close collaboration with the following scientific leaders and their groups:

- Prof. Satoshi Kamiyama Meijo University (MU) Japan

### Carrier lifetime characterization by $\mu$ PCD

- Prof. Vytautas Grivickas Vilnius University (VU) Lithuania

### Theoretical simulations, optical and electrical investigations

- Dr. Masashi Kato Nagoya Institute of Technology (NIT) Japan

### PEC water splitting cell fabrication, characterizations and efficiency evaluation

- Dr. Haiyan Ou                      Demark Technical University(DTU)                      Denmark

### *Fabrication of the nanostructured surfaces in 3C-SiC*

## **7. EQUIPMENT RELEVANT FOR THE PROJECT**

We have available a reactor for growth of p-type 3C-SiC, undoped and nitrogen doped 3C-SiC. The main characterizations tools are available *in house*: AFM, XRD, SEM, TEM LTPL, TRPL, micro-PL and CL spectroscopy, standard Hall, IV, CV, and DLTS techniques. Other characterization tools are available in collaboration (see section 6) as research exchange where the main applicant will visit the partners.

## **8. OTHER FUNDING**

The research field has no funding since it is a new line of research.

## **9. SIGNIFICANCE**

This project initiates a new research field of photoelectrochemical water splitting into H<sub>2</sub> based on 3C-SiC as a photoelectrode. It opens up the possibility to develop a technology in Sweden on 3C-SiC photoelectrochemical water splitting devices for the generation of H<sub>2</sub>. Harvesting solar energy to produce H<sub>2</sub> on a large scale could solve the problems of the depletion of fossil fuels, the emissions of CO<sub>2</sub>, the environmental pollution, and the energy security of our society.

## **10. INDEPENDENT LINE OF RESEARCH**

Previous research in the group of Mikael Syväjärvi has focussed on fluorescent SiC for LEDs and 3C-SiC towards solar cells. In this project, Jianwu Sun initiates a new research of photoelectrochemical water splitting based on 3C-SiC.

## **11. TYPE OF EMPLOYMENT**

Jianwu Sun is now being recruited (start June 2014) to Linköping University for a permanent position as senior researcher engineer (Förste Forskningsingenjör).

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