

# Investigations of a-Si<sub>1-x</sub>C<sub>x</sub> Thin Films as a Catalyst for CO<sub>2</sub> Photoelectrochemical Reduction

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In this work we investigated the catalytic property of amorphous silicon carbide (a-SiC) and SiC loaded copper (Cu-SiC) thin films as photocathodes for the photoelectrochemical reduction of CO<sub>2</sub>. The formers (a-SiC) were elaborated by magnetron sputtering method on both *p*-type silicon (*p*-Si) and glass substrates. The Cu-surface modification of a-SiC (Cu-SiC) thin films were well carried out by Cu particles deposited by evaporation method on the surface of the SiC thin films. The catalytic activity was studied for both simple a-SiC and Cu-surface modified SiC thin films. The results showed that the Cu-modified a-SiC speeds up the photocatalytic activity compared to the unmodified a-SiC. The conduction band is suitably positioned with respect to the CH<sub>3</sub>OH/CO<sub>2</sub> leading to a good reduction of CO<sub>2</sub> using visible irradiation.

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## 1. Introduction

The major environmental concern in the twenty first century is global warming and carbon dioxide CO<sub>2</sub> is its main contributor [1]. To reduce the CO<sub>2</sub> concentration, several approaches have been proposed [2]. One of the most favorable and advantageous methods is the conversion of CO<sub>2</sub> into valuable fuel with the assistance of sustainable energy source such as sunlight [3]. Photo(electro)chemical conversion of CO<sub>2</sub> into small organic molecules with high energy density, such as formic acid and methanol, can contribute both to reduce the atmospheric levels of greenhouse gases, and at the same time, produce carbon neutral fuels and valuable industrial chemicals [4]. Finding suitable materials for photoelectrodes would be critical in the development of such green technology.

Silicon carbide (SiC) is a wide band gap semiconductor with good chemical stability [5–9]. Depending on its crystal structure, the band gap of the SiC varies from 2.4 to 3.4 eV [10]. Moreover, the band structure of SiC can meet the requirements for water splitting [11]. The conduction band edge of SiC is located above the redox energy of the H<sub>2</sub>O/H<sub>2</sub> couple, and its valence band edge is below the redox energy of the O<sub>2</sub>/H<sub>2</sub>O couple [12]. Considering these advantages of SiC, it is worthwhile to fabricate efficient and stable photoelectrodes with favorable structures of SiC. Actually, such investigations have already been in progress. Powder and film of the SiC have been employed as photocatalyst for water splitting and CO<sub>2</sub> reduction [13, 14]. Thus, elaboration of amorphous

SiC thin films with specific selectivity and catalytic properties remains an interesting research field for developing a photocatalyst for CO<sub>2</sub> reduction application.

In this contribution the focus is on the structural, optical, and photocatalytic properties of amorphous SiC (a-SiC) and Cu-SiC thin films, prepared by radiofrequency magnetron sputtering technique in order to study their catalytic power for the reduction of CO<sub>2</sub>. The properties are investigated by SEM and photoelectrochemical measurements.

## 2. Experimental part

Amorphous silicon carbide thin films have been deposited onto monocrystalline bore doped silicon (*p*-Si(100) of resistivity between 1 and 10 Ωcm) and ordinary glass using radiofrequency (RF 13.56 MHz) magnetron sputtering method.

During deposition, distance between the 6H-SiC target, and substrate holder was 9.00 cm, and argon flow was maintained to 4.00 sccm. The total pressure in the chamber was  $1 \times 10^{-2}$  mbar. A voltage is applied to the magnetron cathode, imposing a fixed working power of 150 W. Deposition was made at room temperature for 180 min. The deposition conditions of a-SiC thin films are given in Table I.

Deposition parameters of a-SiC thin films. TABLE I  
 $P_{avt}$  — pressure at the beginning,  $P_{pend}$  — pressure during the deposition.

Debit [sccm] Ar (100%) N60	Distance [cm]	$P_{avt}$ [mbar]	$P_{pend}$ [mbar]	Power [W]	Deposition time [min]
4	8	$6 \times 10^{-6}$	$1.05 \times 10^{-2}$	150	180

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The Cu-surface modification of a-SiC (Cu-SiC) thin films were carried out by copper particles deposited by evaporation method.

### 3. Results and discussion

#### 3.1. SEM characterizations

SEM observation of the elaborated samples of a-SiC thin films revealed a perfect homogeneous morphology (Fig. 1a). The Cu particles are well observed on the SiC surface (as it is shown in Fig. 1b and c).

#### 3.2. Photoelectrochemical activity

##### 3.2.1. Linear sweep voltammetry measurements

The study was carried out using a potentiostat VMP3. The electrochemical cell was assembled with three electrodes system: gold wire as counter electrode (CE), saturated calomel electrode as reference, and a-SiC and (or Cu-SiC) thin film with  $0.5 \text{ cm}^2$  area as working electrode (WE). All the chemicals used were of reagent grade. In the current–voltage ( $I$ – $V$ ) measurements, the voltage scan was kept constant in the  $-1.5/ + 0.5 \text{ V}$  range and the scan rate was  $20 \text{ mV/s}$ . The electrical contact was ensured by the copper circular flat foil at the bottom of the PEC cell. There was no need for conducting silver paint to paste the SiC sample on the copper electrode. The experiments were performed in alkaline ( $\text{pH} = 11$ ,  $0.1 \text{ M Na}_2\text{CO}_3$ ) electrolyte. The experiments were carried out both in dark and under light. The temperature of the electrolytes was kept constant at  $25^\circ\text{C}$ .

In our investigation, when the Cu/SiC catalysts were exposed to visible light, the photogenerated electron–hole pairs were created (Fig. 2).

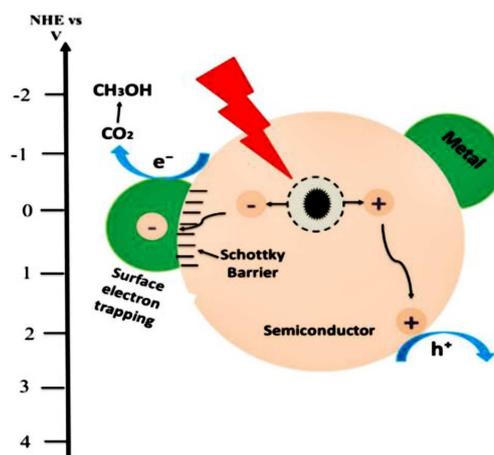


Fig. 2. Schematic reduction activity of  $\text{CO}_2$  to methanol over Cu/SiC photocatalyst under visible light irradiation.

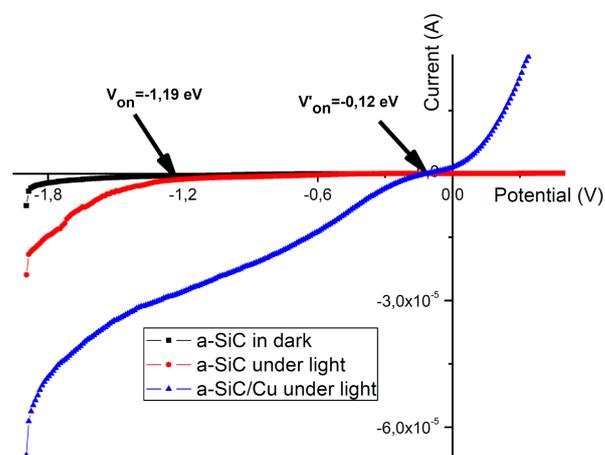


Fig. 3. Current–potential plots of a-SiC thin film in  $\text{Na}_2\text{CO}_3$  electrolyte ( $0.1 \text{ M}$ ) in the dark and under illumination using white light  $100 \text{ W}$  lamp.

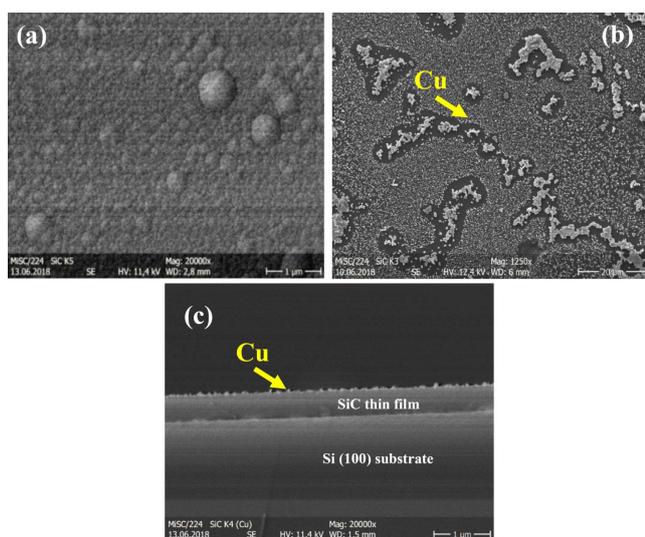


Fig. 1. SEM pictures of an amorphous SiC thin film sample (a) plan view and Cu-SiC thin film sample (b) plan and (c) sectional view.

The voltammogram in Fig. 3 is in agreement with previous reports [15, 16] that reported a similar LSV (linear sweep voltammetry) pattern in  $\text{CO}_2$  saturated-solution in absence and presence of Cu. As proposed by Schouten et al. [17] the cathodic current during LSV might be due to the water reduction generating proton which at higher potential may combine with adsorbed  $\text{CO}_2$  to form different hydrocarbons, such as methanol, methane, formaldehyde, formic acid, etc. The cathodic current further increases with the increase in applied potential. The positive shift in the onset potential by  $\approx 1 \text{ V}$  under light compared to that without light suggests the higher efficiency of  $\text{CO}_2$  reduction under visible light irradiation.

##### 3.2.2. Cyclic voltammetry measurements

Figure 4 shows the voltammogram of a-SiC electrode in  $\text{CO}_2$ -saturated  $\text{Na}_2\text{CO}_3$  solution with and without Cu under visible light illumination. It can be seen that

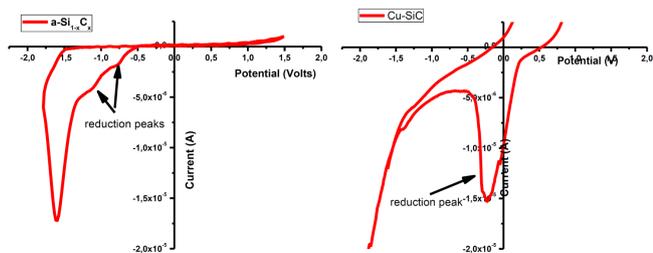


Fig. 4. Cyclic voltammograms of  $a\text{-SiC}$  thin film and  $\text{Cu-SiC}$  thin film in  $\text{CO}_2$ -saturated  $0.1\text{ M Na}_2\text{CO}_3$ .

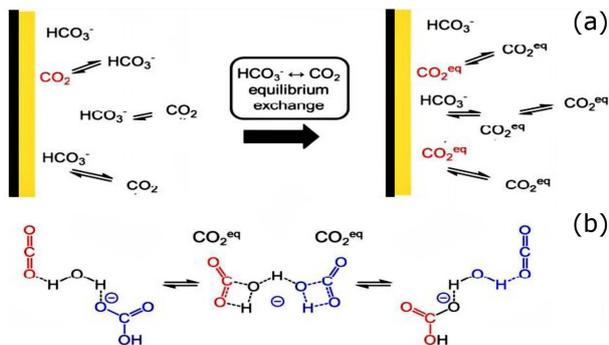


Fig. 5. (a) Proposed equilibrium between  $\text{CO}_2$  and bicarbonate. Red, black, and blue colors indicate atoms that were initially part of  $\text{CO}_2$ , water, and bicarbonate, respectively. (b) Schematic of the proposed mechanism for increasing the effective  $\text{CO}_2$  ( $\text{CO}_2(\text{eq})$ ) concentration via the equilibrium between  $\text{CO}_2$  and bicarbonate. Species at the  $\text{Cu}$  surface that can be readily reduced are marked in red.

when  $a\text{-SiC}$  thin film was used, two reduction peaks were produced, while a pronounced reduction peak appeared which at  $E = -0.38\text{ V}$  could be due to the reaction of  $\text{CO}_2$  with protons and electrons leading to the formation of  $\text{CH}_3\text{OH}$  ( $E_{\text{CO}_2/\text{CH}_3\text{OH}} = -0.38\text{ V}$ ), as reported in [18].

The shape of the voltammogram in absence of  $\text{Cu}$  presents a regular cycle where the cathodic current increases with the increase of applied potential above  $-0.8\text{ V}$  which may arise from water/proton reduction [15, 19]. In presence of  $\text{Cu}$ , a strong peak was observed in the voltammogram at  $-0.38\text{ V}$  for  $\text{Ag}/\text{AgCl}$  under light irradiation and a weak peak in the anodic current was evident at  $0.6\text{ V}$  for  $\text{Ag}/\text{AgCl}$ .

The majority of the  $\text{CO}_2(\text{aq})$  being reduced is actually supplied by  $\text{HCO}_3^-$  through rapid equilibrium (Fig. 5), and the primary role of  $\text{CO}_2(\text{g})$  is to establish and maintain the equilibrium concentration of  $\text{CO}_2(\text{aq})$  based on other species in solution. Rapid equilibrium exchange between  $\text{CO}_2(\text{aq})$  and  $\text{HCO}_3^-$  in solution could increase the effective  $\text{CO}_2(\text{aq})$  concentration ( $\text{CO}_2(\text{eq})$ ) near the electrode surface by allowing  $\text{CO}_2(\text{aq})$  to hop between bicarbonate ions in solution (analogous mechanism for proton diffusion in water in which protons hop between water molecules), essentially allowing any  $\text{HCO}_3^-$  near the surface to be reduced in the  $\text{CO}_2(\text{eq})$  form (Fig. 5).

The role of bicarbonate is not simply a  $\text{pH}$  buffer 11 or  $\text{H}^+$  donor for  $\text{CO}_2$  reduction as previously proposed, but also key to the reaction rate by facilitating  $\text{CO}_2(\text{aq})$  transportation due to its much higher concentration. It is important to clarify that this hypothesis is fundamentally different from claiming that bicarbonate is equivalent to  $\text{CO}_2$  in the  $\text{CO}_2\text{RR}$  and can therefore be reduced directly at the electrode surface. If either  $\text{CO}_2(\text{eq})$  moiety of the bicarbonate/ $\text{CO}_2$  equilibrium complex (Fig. 5) is reduced in the  $\text{CO}_2\text{RR}$ , the other moiety is simultaneously converted to  $\text{HCO}_3^-$  and can no longer be directly reduced. Considering that this rapid equilibrium is a solution-mediated, rather than electrode-mediated process, and the similarity of isotopic labelling results on other  $\text{CO}/\text{selective}$  electrodes, the proposed role of bicarbonate is likely to be general on all  $\text{CO}_2$  reduction. This proposed mechanism is in good agreement with previous reports that state that  $\text{CO}_2\text{RR}$  rates are significantly higher in bicarbonate solutions than in other buffer solutions at the similar  $\text{pH}$  and potential.

#### 4. Conclusion

On the basis of our findings, it could be postulated that the addition of  $\text{Cu}$  to  $a\text{-SiC}$  can alter the catalytic properties and overall efficiency of the  $\text{SiC}$  thin films. The incorporation of  $\text{Cu}$  as a charge-carrier trap seems to enhance the reaction rate and also increase the lifespan of separated electron-hole pairs.

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#### References

- [1] M. Heima, R. Luo, R.T. Haasch, J.I. Gold, M. Yamauchi, P.J. Kenis, *J. Am. Chem. Soc.* **139**, 47 (2016).
- [2] T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **277**, 637 (1979).
- [3] L. Kimfung, D. Martin, T. Junwang, *Chin. J. Catal.* **32**, 879 (2011).
- [4] D.D. Zhu, J.L. Liu, S.Z. Qiao, *Adv. Mater.* **28**, 3423 (2016).
- [5] H. Morkoc, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov, M. Bums, *J. Appl. Phys.* **76**, 1363 (1994).
- [6] P.G. Neudeck, *J. Electron. Mater.* **24**, 283 (1995).
- [7] J.B. Casady, R.W. Johnson, *Solid State Electron.* **39**, 1409 (1996).
- [8] G. Demir, T.E. Renfro, R. Glosser, S.E. Sadow, *J. Appl. Phys. Lett.* **84**, 3540 (2004).
- [9] Q.Z. Zhao, F. Ciobanu, S. Malzer, L. Wang, *J. Appl. Phys. Lett.* **91**, 121107 (2007).
- [10] S. Kaci, R. Rahmoune, A. Boukezzata, et al., *J. Nanoelectron. Optoelectron.* **14**, 1002 (2019).

- [11] R. Memming, *Electrochim. Acta* **25**, 77 (1980).
- [12] C.H. Park, B.H. Cheong, K.H. Lee, K. Chang, *Phys. Rev. B* **49**, 4485 (1994).
- [13] D.H. Van Dorp, N. Hijnen, M.D. Vece, J.J. Kelly, *Angew. Chem. Int. Ed.* **48**, 6085 (2009).
- [14] F. Azzouz, S. Kaci, I. Bozetine, A. Keffous, M. Trari, S. Belhousse, S. Aissiou-Bouanik, *Acta Phys. Pol. A* **132**, 479 (2017).
- [15] Q. Shen, Z. Chen, X. Huang, M. Liu, G. Zhao, *Environm. Sci. Technol.* **49**, 5828 (2015).
- [16] Y. Hori, A. Murata, R. Takahashi, *J. Chem. Soc.* **85**, 2309 (1989).
- [17] M. Ren, K. Valsaraj, *Int. J. Chem. React. Eng.* **7**, (2009).
- [18] P. Usubharatana, D. Mc Martin, A. Veawab, P. Ton-tiwachwuthikul, *Ind. Eng. Chem. Res.* **45**, 2558 (2006).
- [19] M. Tahir, B. Tahir, N.A.S. Amin, H. Alias, *Appl. Surf. Sci.* **389**, 46 (2016).