

PHOTOELECTROCHEMICAL METHODS FOR SEMICONDUCTOR DEVICE PROCESSING

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Abstract—The usefulness and capabilities of photoelectrochemical processing of III-V semiconductors is presented. Examples include the etching of small period gratings, the formation of integral lenses, the decomposition of small bandgap semiconductors, the etching of p-type semiconductors, and the photoinitiated deposition of metal. The transport of carriers in the semiconductor and reactivity of the surfaces is discussed.

Key words: photoelectrochemistry, semiconductors, chemical etching, indium phosphide, gallium arsenide, indium arsenide.

INTRODUCTION

Throughout the evolution of the semiconductor industry, electrochemistry has been an active area of investigation because it is the basis for many processes used in the fabrication of semiconductor devices. Wet etching, electrodeposition, oxide formation, corrosion and defect etching are some of the electrochemical processes.

The growth in the variety of III-V compound semiconductor devices for optoelectronic, high speed electronic and microwave applications presents opportunities for new processing methods[1]. Photoelectrochemical (PEC) processing is of interest because it can provide unique capabilities which result from involving both the electronic and optical properties of the semiconductor in the reaction sequence. Thus, any change in the electrical or optical properties can be used as the basis for selective processing. There are several advantages of PEC techniques which can be used in device processing: PEC processing uses relatively low energy reactants (*eg* visible light) so that damage free processing can be achieved[2]; the rate of reaction is often directly proportional to the light intensity so spatial variations in the rate can be easily achieved[3]; PEC processing can be made bandgap selective for multi-layered heterostructures by restricting the wavelengths of the illumination; since minority carriers are used to initiate the reaction sequence, n/p dopant selectivity can be achieved; the reactions can be made sensitive to changes in the energy level of the conduction or valence band edges; perturbations in the optical or electrical properties of the semiconductor which lead to recombination or electron-hole generation can be used for defect analysis; since the electrical current and illumination intensity are directly proportional to the rate of reaction and can be measured, the process is easily monitored; and PEC processing and facilities are relatively simple and non-hazardous.

In this paper, five PEC reactions will be discussed and used to illustrate the limitations and future opportunities.

OXIDATIVE DECOMPOSITION OF n-TYPE SEMICONDUCTORS

The most common and simplest form of PEC processing is the photo-oxidative decomposition of n-type semiconductors, as shown in Equation (1) for n-InP.

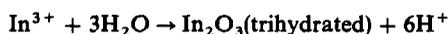


where h^+ is a valence band hole and e^- is a conduction band electron. The total number of electron transfer steps in Equation (1) is six which can vary depending on the semiconductor and the conditions. Holes which are photogenerated within the semiconductor under reverse bias conditions migrate to the solution interface and initiate the decomposition reaction. The hole concentration in the semiconductor can be determined from the transport relation for the hole current, J_p , and the continuity equation, as shown in Equations (2) and (3), respectively[4]

$$J_p = q\mu_p pE - qD_p \nabla p \quad (2)$$

$$\frac{dp}{dt} = -\frac{1}{q} \nabla J_p + G_p - R_p, \quad (3)$$

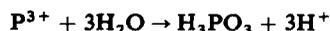
where q is the magnitude of the electronic charge, μ_p is the hole mobility, E is the electric field, D_p is the hole diffusion coefficient, G_p is the generation rate and R_p is the recombination rate. Once the electrochemical reaction in Equation (1) has been initiated, In and P are oxidized to the 3+ valence state and can undergo following chemical and electron transfer reactions in solution[5, 6]



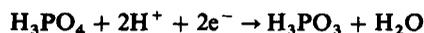
$$\log[\text{In}^{3+}] = 8.65 - 3\text{pH} \quad (4)$$



$$\log\left[\frac{[\text{InOH}^{2+}]}{[\text{In}^{3+}]}\right] = -3.88 + \text{pH} \quad (5)$$



$$(6)$$



$$E = -0.276 \text{ V.} \quad (7)$$

Thus, the photo-oxidation of InP involves the transport of thermally and photogenerated holes within the semiconductor to the solution interface, transport of reactants within the solution to the interface, solvation of the reaction products and transport of the reaction products into the bulk of the solution.

The formation of surface relief features in III-V semiconductors is particularly useful. PEC etching is a useful technique because the rate of etching is directly proportional to the intensity over a wide range. One structure of interest is the formation of surface relief diffraction gratings[7]. The hole transport equations for PEC etching have been used to examine the effect of several variables on the spatial resolution of the process for etching diffraction gratings in n-InP[8]. In the analysis, a sinusoidal spatial variation in light intensity was used to illuminate the surface.

$$G_p = \frac{\alpha I_0}{h\nu} e^{-\alpha x} \left(1 + \cos \frac{2\pi y}{L} \right), \quad (8)$$

where I_0 is the average intensity transmitted in to the semiconductor at $x = 0$, α is the absorption coefficient and y is the distance along the surface. The solution transport and solvation effects were expressed as a first order rate, $Kp(0, y)$, where $p(0, y)$ is the concentration of holes at the interface and K is the first order rate constant (centimeters per second) and is also referred to as a reaction velocity. Table 1 shows the calculated values of K for n-InP. As the period of the diffraction grating is made smaller, the resolution of the etching, or ability to replicate the sinusoidal variation in light intensity, is limited by the velocity of the chemical reaction, K . When K is small, as in the case of HF, the photogenerated holes can undergo surface diffusion and reduce the spatial resolution. The velocity of the chemical reaction can be increased by choosing electrolytes which have higher solubilities for the reaction products. If the velocity were limited by the precipitation of one or more of the reaction products, then the maximum diffusion controlled current can be estimated by Equation (9)

$$i_{lim} = \frac{nFA(D_0 C^*)^{1/2}}{(\pi t)^{1/2}} \quad (9)$$

where i_{lim} is the limiting current density as a function of time, F is Faraday's constant, n is the number of equivalents per mole, A is the area, D_0 is the diffusion coefficient, t is the time and C^* is the maximum concentration at the electrode surface and can be approximated by the solubility product, K_{sp} .

The limiting current, i_{lim} , has also been increased by raising the temperature of the electrolyte. The K_{sp}

of the reaction products would be expected to increase significantly for the species of interest here. Also, the diffusion coefficient follows the general form $D_0 \propto T/\eta$, where η is the viscosity of the solvent[9]. The viscosity for water follows the form $\ln \eta = A + B/T$, so that D_0 increases as Te^{-T} . The increase in the spatial resolution of submicrometer diffraction gratings with temperature for n-GaAs has been observed[10].

Relatively large surface relief features ($eg > 10 \mu m$) can be etched in n-type semiconductors by producing a spatial variation of light intensity across the semiconductor surface. Integral lenses have been etched into InP/InGaAsP light emitting diodes for the efficient coupling of light into optical fibers by projecting the image of a photomask onto the surface of the semiconductor[11]. Although the spatial resolution of the PEC process is adequate, the optical quality of the resulting surface is very important. In order to achieve surfaces with a smoothness on the order of $\lambda/4$, the preferential etching of more reactive crystal planes must be eliminated and the relative rate of the dissolution products should be similar. This has been achieved by using HF as the electrolyte where reaction velocity is relatively slow and preferential complexation does not occur. Thus, high spatial resolution (large reaction velocity) and uniform dissolution achieved through slow reaction velocities can be conflicting requirements.

SMALL BANDGAP SEMICONDUCTORS

The bandgap of n-InP, 1.35 eV, results in relatively few thermally generated holes at room temperature so that a very large photoetch rate can be achieved compared with the dark etch rate. Smaller bandgap semiconductors, such as InAs, are of great interest because of their mobility and the large band edge discontinuities that can be achieved with lattice matched materials such as GaSb. However, the small bandgap of InAs, 0.36 eV at room temperature, results in a significant concentration of thermally generated holes, as shown in Table 2.

The electrochemical current-voltage behavior of n-InAs and p-InAs in 0.2 M H_2SO_4 is shown in Fig. 1. The oxidation current increases dramatically at potentials positive of 0.1 V vs. *sce* and is independent of dopant type. Although a depletion region is formed within both semiconductors at potentials positive of 0.1 V, holes are still available at the semiconductor-solution interface to participate in the dissolution of the crystal. The equilibrium concentration of holes for heavily doped n-InAs is large

Table 1. Values of the reaction velocity K for PEC etching of InP as determined from the experimental holographic sensitivity data in Refs [7] and [8]

Electrolyte	$K/cm s^{-1}$
2 M HCl	8.9×10^2
1.5 M HF, 0.5 M KF	6.3×10
2 M HBr	1.5×10^3
1.5 M H_2SO_4	1.5×10^3

Table 2. Room temperature values for n-InAs and p-InAs

	p-InAs	n-InAs
Dopant density/cm ⁻³	2×10^{17}	1.8×10^{16}
Mobility/cm ² V s ⁻¹	290	24,700
D_0 cm ² s ⁻¹	645	8
Saturation current A cm ⁻²	16.6	44.2

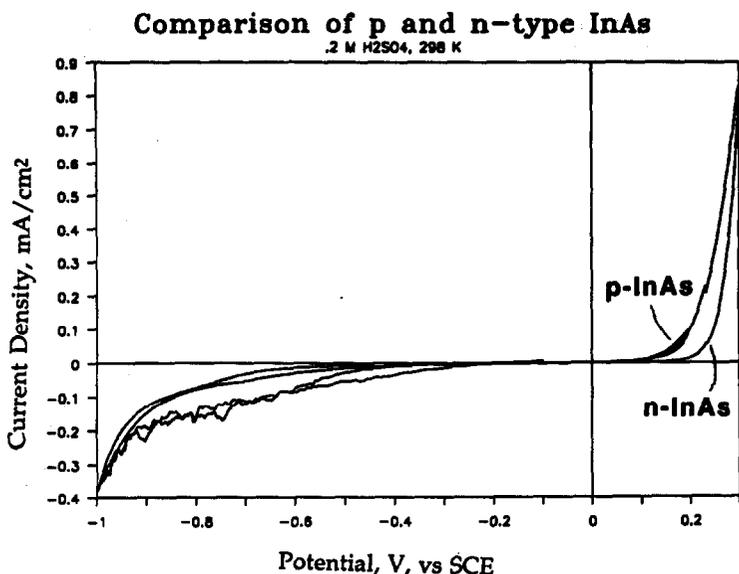


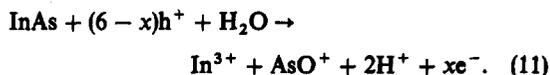
Fig. 1. Current density vs. potential for n-InAs and p-InAs in 0.2 M H₂SO₄ at 25°C.

because of the small bandgap. The saturation current, J_{sat} , is much greater than for larger bandgap semiconductors, Equation (10)[4]

$$J_{sat} \approx \frac{qD_p p_{n0}}{L_p}, \quad (10)$$

where L_p is the diffusion length for holes and p_{n0} is the equilibrium concentration of holes in the n-type semiconductor. Since the thermal generation of minority carriers and saturation current are large, the surface concentrations of carriers within the semiconductor and at the solution interface are always in thermal equilibrium. Since the oxidation of the lattice has a first order dependence on the hole concentration at the interface, $p(0, t)$, the etching of

the lattice, Equation (11), is independent of dopant type (n or p) in the potential region between the flat band potential of n-InAs and p-InAs:



It also means that the potential region of low dark current that is usually observed with n-type III-V semiconductors and used for the selective PEC etching is not achievable here. Figure 2 shows the effect of pulsed illumination on an n-InAs electrode in 0.2 M H₂SO₄. The photoanodic current is observed at potentials positive of the flat band potential (V_{fb}) which is 0.1 V. The increase in the anodic current with light is a result of the non-

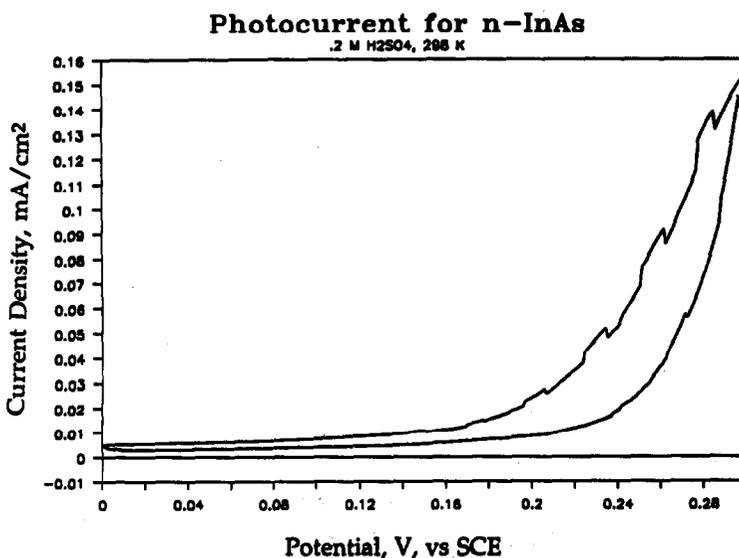


Fig. 2. Current density vs. potential for n-InAs when illuminated with a pulsed He-Ne laser.

InAs Hole and Current Ratios
325°K/275°K

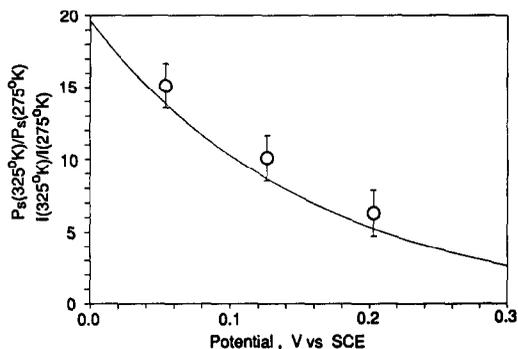


Fig. 3. Ratio of the hole concentration at the semiconductor-solution interface for two temperatures vs. potential (solid line) and ratio of the observed current for two temperatures vs. potential (circles).

equilibrium photogeneration of holes. Thus, the selectivity of the photoetching for small bandgap semiconductors is limited by the quantity $[p(0, t) + \Delta p(0, t)]/p(0, t)$, where $\Delta p(0, t)$ is the photo-generated hole concentration at the solution interface.

At lower temperatures, the thermal generation of minority carriers is decreased and the equilibrium concentration of holes in n-InAs is smaller. Figure 3 shows the calculated ratio of the equilibrium concentration of holes at the semiconductor-solution interface at two temperatures vs. potential. Thus, at more negative potentials and lower temperatures, a larger $[p(0, t) + \Delta p(0, t)]/p(0, t)$ ratio is expected. The experimental results for the ratio of the oxidation currents at two temperatures vs. potential are also shown in Fig. 3. The actual light-to-dark etch rates follow the current ratio data shown in Fig. 3 where the most desirable values occur at low temperature and negative potentials.

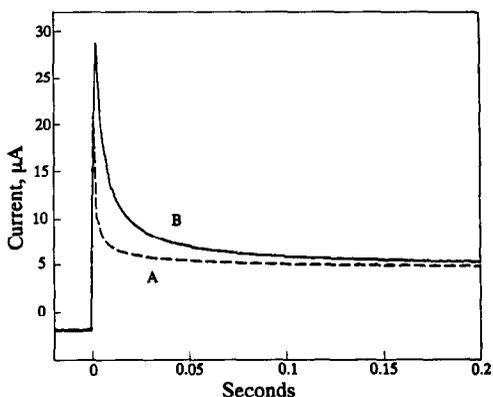
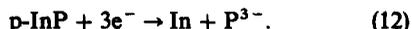


Fig. 4. Current-time response for a potential step from -0.8 – -0.1 V vs. sce for (100) p-InP in 0.5 M H_2SO_4 at $66^\circ C$. Curve A with no illumination and B illumination for 0.1 , 50 s prior to the potential step.

p-TYPE PEC ETCHING

A major difficulty in the PEC etching of multilayered structures is that many p-type semiconductors cannot be selectively etched. This is because conduction band electrons, which are the minority carriers in p-type semiconductors, do not directly lead to the dissolution of the crystal lattice. A two-step PEC process for p-InP has been investigated[12]. The semiconductor is first stepped to a potential, V_{cat} , where the semiconductor can be photoreduced, Equation (12):



The potential is then stepped to a value, V_{an} , where the insoluble products of the photoreduction are oxi-

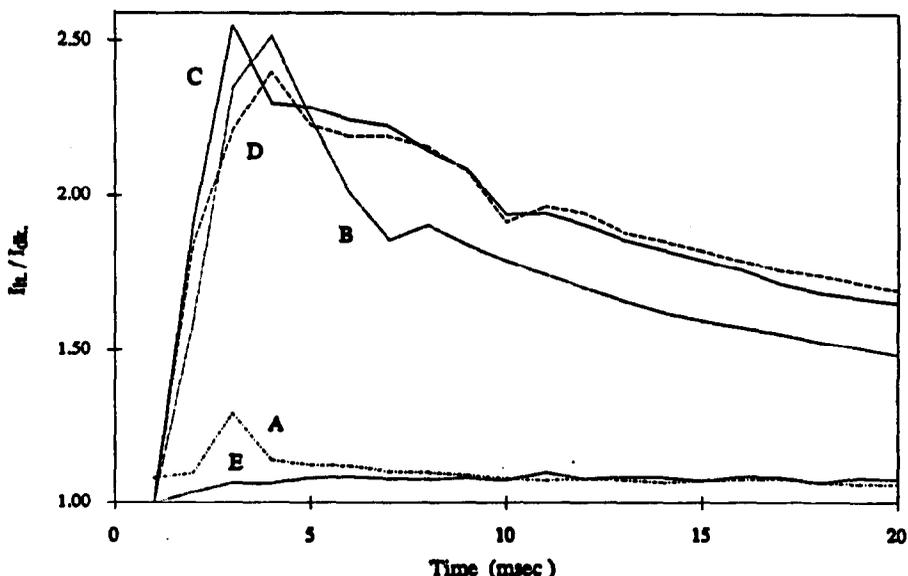
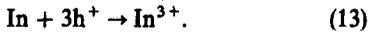
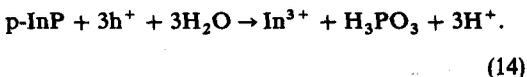


Fig. 5. Plot of the net current, $I(\text{dark})-I(\text{illuminated})$, for (100) p-InP at $49^\circ C$ in 0.5 M H_2SO_4 when the potential was stepped from (A) -0.2 V, (B) -0.6 V, (C) -0.8 V, (D) -1.0 V and (E) -1.4 – -0.1 V. The electrode was illuminated 50 s prior to the potential step by a He-Ne laser for 0.1 s.

dized by majority carriers, Equation (13):



By repetitively stepping the potential from one where the photoreduction occurs to one where the oxidation is feasible, p-InP can be photoetched. Figure 4 shows the chronoamperogram for p-InP at 0.1 V vs. sce having been stepped from -0.8 V. In curve A of Fig. 4, the p-InP was kept in the dark for the entire time while at -0.8 V. In curve B, the InP was illuminated for 0.1 s while at -0.8 V. The increase in the anodic current from curves A to B is due to the oxidation of the products formed during the photoreduction of the surface, Equation (12). During the experiment, the electrode was allowed to sit at open circuit for 60 s following the illumination at -0.8 V so that any soluble products could dissolve and be transported away from the electrode surface. Figure 5 shows the net current, $I_{\text{illum}} - I_{\text{dark}}$, from the chronoamperogram (Fig. 4) as the potential is stepped to more negative values of V_{cat} . If V_{cat} is too positive, then the reduction reaction does not proceed to completion as shown in curves A and B. If V_{cat} is too negative, then the reduction reaction proceeds in the dark as shown in curve E. Figure 6 shows the effect of V_{an} on the current ratio, $I_{\text{illum}}/I_{\text{dark}}$, from the chronoamperograms. If V_{an} is too negative (curve A), holes are not available to carry out the oxidation reaction, Equation (13). If V_{an} is too positive, then the concentration of holes is too large and the decomposition of p-InP, Equation (14) is observed.



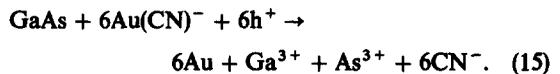
Thus, the hole oxidation of the insoluble products as a result of the photoreduction occurs preferential to the oxidation of the semiconductor lattice, Equation

(14). The dissolution of products can be improved with temperature and etch rates in excess of $1 \mu\text{m min}^{-1}$ have been observed.

PEC INITIATED REACTIONS

The photogeneration of electron-hole pairs in III-V semiconductors can be used to initiate reactions other than the decomposition of the lattice. The use of photogenerated carriers as the driving force for the reaction has several advantages: (1) electrically isolated areas can be processed because no electrical contact is required; (2) the rate of the chemical reaction is controlled by the intensity of the illumination; (3) the extent of the chemical reaction can be controlled by one of several parameters such as the volume of material to be oxidized; (4) a variety of chemical reactions, with potential or chemical selectivity, can be utilized.

One example, the PEC deposition of gold *via* connections for GaAs field effect transistors, has been demonstrated[13]



Photogenerated electron-hole pairs in GaAs initiate the dissolution of the semiconductor crystal. Electrons migrate into the bulk of the semiconductor and reduce the gold cyanide complex at the source contact of the FET. Thus, through-wafer, front to back *via* connections are metallized without making electrical contact and without forming voids in the metal fillet. The electrochemical potential of the gold reduction is important because a depletion region is needed within the semiconductor so that holes

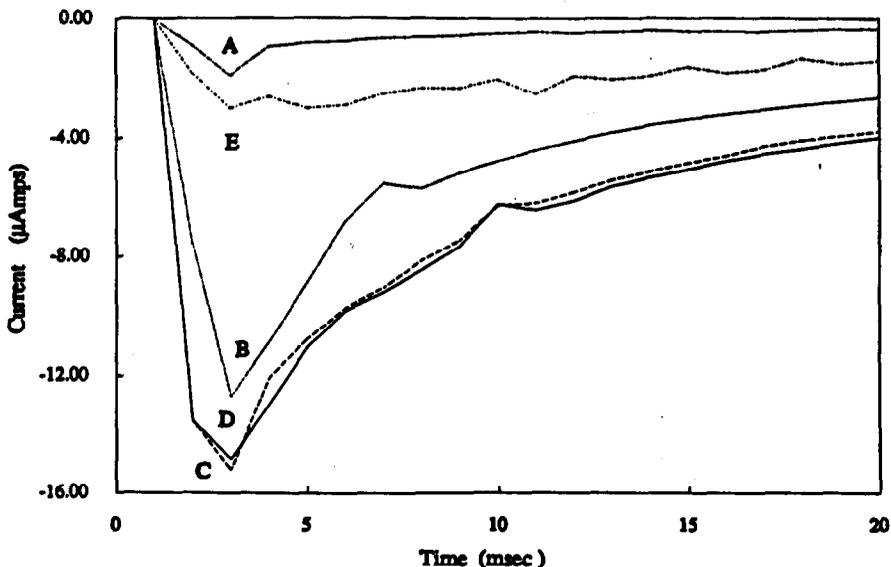


Fig. 6. Ratio of the $I_{\text{illum}}/I_{\text{dark}}$ for (100) p-InP at 49°C in $0.5 \text{ M H}_2\text{SO}_4$ for a potential step from -0.8 V to (A) 0 V, (B) 0.1 V, (C) 0.2 V, (D) 0.4 V and (E) 0.5 V. The electrode was illuminated for 0.1 s by a He-Ne laser 50 s prior to the potential step while poised at -0.8 V.

migrate to the semiconductor-solution interface and electrons migrate to the metal-solution interface.

SUMMARY AND FUTURE TRENDS

The photoelectrochemical effects in semiconductors provide several valuable tools for fabricating semiconductor devices. The ability to etch spatially selective features has been demonstrated for a wide range of bandgaps and for both n-type and p-type semiconductors. The use of light to selectively deposit metals has also been demonstrated.

The spatial resolution of PEC etching is limited to features in the 0.1–1.0 μm range, by the rate of the chemical reactions. Research to improve the spatial selectivity of PEC etching by optimizing the electrolyte conditions is ongoing. Multilayered materials present other challenges for PEC etching. The spatial and depth resolution for specific changes in the bandgap (wavelength selectivity) or band structure (conduction band or valence band changes at heterojunctions) have not been extensively investigated. More recent high-speed electronic multilayered structures have layer thicknesses less than the absorption depth of light or the depth of typical depletion regions. The PEC characteristics and selectivity in such materials can be significantly different. The resolution of PEC etching of graded multi-layers (eg graded values in $\text{Ga}_x\text{Al}_{1-x}\text{As}$) is also of interest. The ability to stop etching at any of the specific layers in a multi-layered III-V integrated optoelectronic device is potentially of great value.

Finally, there is a large variety of chemical reactions which can be photoinitiated on III-V semicon-

ductors to provide unique materials or processing capabilities. The photoinitiated chemical reactions for depositing metals, passivation materials or selective chemical reactions is a relatively untapped area.

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