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Thin Metal Films Used for Enhancing PV Cell Efficiency

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Metalnanodimensionstructureshavemultipleapplicationsinmoderntechnology.Noncontinuousthinislandmetalfilms ofseveraltypes of metals deposited on dielectric or semiconductor surface introduce a unique behavior. In response to light exposure incertainrange,themetalislandspresentaresonantabsorptionoflightaccompaniedwithacollectivebehavioroffreeelectronsintheseislands.Inthispaper,wepresentoneofthepossiblewaystoincreasetheefficiencyofsolarcellswithmetalislandsimbeddedin a semiconductor junction. Rough calculation was performed for a silicon solar cell and showed an increase of 17.5% in the overallefficiencyofthecell.

INTRODUCTION

Solarcells,asalternativeenergysources,attractmuchatten-tion in recent decades due to enormous energy obtained byearthfrom thesun, about 1.2×10^{17}W. Solarcells have thepotentialtoreplacefossilfuelsasthemainmeansofelectric power generation. However, solar cells of all types suffer fromtwo main deficiencies: relatively low conversion efficiencyand high cost in comparison with conventional fossil fuelelectric sources. The search of ways to reduce fabrication costsand increase efficiency of photovoltaic devices is the maingoalofresearchersanddevelopers.

Unfortunately, efficiency of solar cells based on semi-conductor materials is limited due to high electrical andoptical losses [1]. Moreover, the luminescence (radiative)recombination further restricts the possible efficiency; thus,the efficiency of silicon solar cells cannot theoretically exceed31%[2].

There are several ways to increase efficiency of solarcells. The first one consists in combining semiconductorphotovoltaic converters with suitable heat absorbing bodiesthat is, water or oil for heat them and use this thermalenergy. This specific method is already applied in industry.However,thismethodrequiresadditionalcapitalinvestmentsandsignificantcomplicationofusedequipment.

The second method to improve efficiency is based onutilizingvarioussemiconductormaterialsinordertoenlargethespectralefficiency.Multijunctiondevices,orheterojunc-tion devices, can reach larger spectral efficiency by capturingdifferentpartsofthesolarspectrum.Amulti-junctiondeviceis a stack of individual single-junction cells in descendingorder of bandgaps. The top cell captures the high-energyphotonsandpassestherestofthephotonsontobeabsorbedby lower-bandgap cells. Sze has shown [3] that consecutivecombinationof36junctionsmayattainanidealefficiencyof72%.ThemainproblemsinestablishingsuchPVcellsarehightechnologicalcomplexityandhighcost,respectively.

Thethirdmethodwehaveinmindtoincreaseefficiencyisusinghotelectronsthatgeneratechargedcarrierswithenergythat is higher than the semiconductor bandgap. It is knownthateachphotonexcitesonlyoneelectron-holepair,andtheexceeding energy dissipates as heat due to thermalizationprocesses. These processes occur since photons cannot splitto two or more particles. However, a “hot” particle maytransfertheexceedingenergytootherfreeparticlesbyimpactand thus to create another electron-hole pairs. Such chainionization impact reaction exists in all semiconductors withvery low efficiency. However, by this way, efficiency maybe increased only using low-dimensional structures such asquantumwells[4],quantumdots[5],ornanocrystalsof

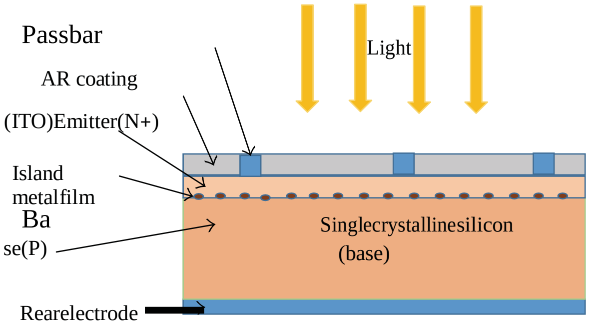


FIgURe1:AsideviewoftheproposedPVsystem.

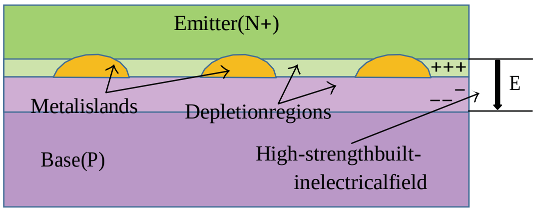


FIgURe2:Animprovedphotovoltaicstructure.

above 5 nm sizes [6]. Detailed analysis of low dimensionalstructuresthatareapplicableforthesolarlightconvertingwasdonebyGreen[7].Itisnecessarytotakeintoaccountthatthecomplicationofthesemiconductorstructurealsoleadstothe SRH(Shockley-Reed-Hall)recombinationincrease.

Thin metal island films represent another type of lowdimensionalstructures.Asknown,suchthinfilmsbuiltfromseveraltypesofmetalshaveaninterestingproperty:in response to light exposure in a certain spectral range, inthe islands of the metal occurs resonant absorption of light.This phenomenon can be explained by the appearance oflocalized plasmons-polaritons with intensity and frequencythatarerelativetothesizeofislandsinthefilm.Thelocalized surface plasmons represent collective behavior offree electrons confined to the small metal particles. In otherwords,surfaceplasmonsarecoherentfluctuationsinelectrondensity, occurring at a “free-electron” metal-dielectric ormetal-air interface. Mie theory and Maxwell-Garnet theoryexplained the surface plasmon resonance (SPR) in terms ofhigher moment oscillation and particle size [8, 9]. It wasfoundthatthewidthandpeakpositionoftheSPRaredepending on the particle size, shape, and environment [10,11].Thus,theeffectoftheSPRcanbeconsideredasasourceof electrons obtained by absorption of fast or high-energyphotons. Obviously, this source of electrons should be usedinsolarcelltechnology.

The metal nanoparticles are utilized to provide extrascattering in order to increase the efficiency of the pho-tovoltaic cells [12] or for the enhancement of photovoltaicdevices [13] by using the surface plasmon resonance withinthe visible and near-visible spectral range. In this paper, wedescribe the novel idea of SPR application for increasingsolarcellsefficiency.Whenaphotonwithsuitableenergyis absorbedbyametalparticle,aplasmonpolaritonarises;thatis,conductingelectronsinthemetalparticlesareexcitedandloginresonance.Energyoftheseexcitedelectronsincreasesandbecomessufficientfortransitiontotheconductingbandof the semiconductor. Thus, each metal island becomes agenerator of free electrons confined within the island. Ourgoal is to create conditions for transition of these additionalelectronstotheconductingbandofthesemiconductor.

1. MechanismofEfficiencyIncreasing:QualitativeAnalysis

Figure 1 presents a side view of our novel photovoltaic (PV)cell. As shown, the PV system looks like a conventional diodestructure; a single crystalline base of the device was chosen forsimplicity of arguments and calculations. There is only onedistinction between usual PV cell and our novel device: anisland metal film is imbedded in the interface between baseandemitter.Theareaofthesemiconductorinthevicinityof this interface is depleted. Therefore, this area is the mostactive part of the diode photovoltaic system. The chargedcarriersgeneratedinthedepletionregionsareseparatedby the built-in electrical field and may be used for electricgeneration.Thus,theelectronsinjectedintothisareawillbeusedwithmaximumefficiency.

A metal island thin film imbedded into the semiconduc-tor P/N structure is shown in Figure 2. The built-in highstrength electrical field inside the depletion zone is shownalso. The main criterion for selection of the metal is its abilityto generate plasmon-polaritons under light absorption anditsenergycompatibilitywiththesemiconductorsurroundingthe metal islets. This criterion limits the range of metalswhich can be used. It could not be transition metals as theabsorption of light in them leads to intraband transition ofexcited electrons and does not form plasmons [11]. Metalswhichcanbeappliedarealkalimetals,alkalineearthmetals,noblemetals,andsemimetals.

The second criterion for selection of metal is the oppor-tunity to create a Schottky diode in contact with the semi-conductor. The second requirement enables us to form a lotof nanodimensionSchottky diodes, each of which is servedas an additional source of electrons. For this purpose, thework functions of metal and semiconductor must satisfy thefollowingrelation:

0▯−0▯/▯>0, (1)

where0▯is the electron work function of the metal and0▯/▯is the electron work function of the semiconductor. Asknown,thisinequalitygeneratesaspace-chargeregioninthesemiconductor and a potential barrier with the height □□$_S$writtenforthen-typesemiconductorasfollows[3]:

□□▯=0▯−□□−(□▯−□▯), (2)

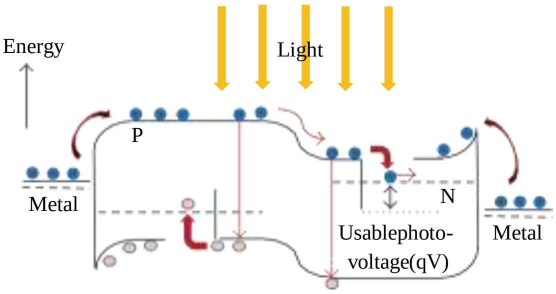
where□□ is the electron affinity or the width of the con-ducting band in the semiconductor, □▯is the bottom of theconducting band, and □▯is the Fermi level for the giventemperature.Here,thedifference(□▯−□▯)isdetermined

□$_{in}$,semiconductorproperties,andthequalityofelectriccontacts[14]:

□=$\frac{□_m}{}$=$\frac{□_m □_m}{}$=$\frac{FF \cdot □_{sc} □_{oc}}{}$, (4)

□$_{in}$

□$_{in}$



□$_{in}$

FIgURe3:AschematicenergydiagramforthenovelPVcell.

by the concentration of dopant atoms in the semiconductor.This way, each metal island forms a Schottky barrier with theemitterandanOhmiccontactwiththebase.

As known, the Schottky diode built on the n-type semi-conductortransferselectronsfromitsemitter(metalpart)to

where□$_m$ is the maximum produced power, □$_m$ and □$_m$ arethe maximum produced current and voltage, respectively, □$_{sc}$and □$_{oc}$are the short circuit current and the open circuitvoltagerespectively,andtheFFisaFill-FactorofthePVcell.

Maximum efficiency of such one-junction solar cell cannotexceedtheShockley-Queisserlimitdependedbythebandgapwidthandthesemiconductorquality[15].

Maximumproducedcurrentmaybecalculatedfromthe basic Shockley equation. This current is described as afunctionofthegeneratedcurrent,□▯[16]:

□$_m$=□($\frac{□▯}{}$−1). (5)

thebase,underexternalpositivebias.Inourcase,thebuilt-involtagecreatedonthep-njunctionofthephotovoltaic

▯ □$_m$

system plays a role in this bias. In order to begin emissionof electrons in the conductive band of the semiconductorfrom metal islands, the electrons in the metal island shouldbe excited. These electrons obtain exciting energy from

thesunlight.Figure3representsaschematicviewoftheenergydiagramforourconstructionunderirradiation.
Under solar light irradiation, the high-energetic photonsabsorbed by the semiconductor generate electron-hole pairswith very-high energy which mainly lost on thermalizationprocesses, thus decreasing the PV cell efficiency. In oursystem, these high-energetic photons are absorbed by themetal nanoparticles to produce plasmon-polaritons. Excitedelectrons from these metal islets are injected into the con-ducting band of the semiconductor due to the resonanceenergyexceedingtheSchottkybarrier.Theseadditionalelectrons will be collected by emitter electrode of the PV cell,thusincreasingthecurrentintheload.

2. MechanismofEfficiencyIncreasing:QuantitativeAnalysis

To approximate calculation, we used the parameters of thesolarcellbasedonthesingle-crystallinesilicon.Thebuilt-involtageinthedepletionregionofthephotovoltaiccell,showninFigures1and2,isdescribedbythewell-knownrelation[3]

□□□□

This current is proportional to the generated current. There-fore,efficiencyofthecellmaybeincreasedbyincreasingthegenerationcurrentorattheexpenseofincreasingtheelectronfluxgeneratedbyPVcell.
As known, only photons with energy higher than thebandgapmaybeabsorbedbysemiconductorwithgenerationof electron-hole pairs. However, most of the photons whichhave energy enough to excite charged carriers produce tooenergetic electron-hole pairs. These charged particles decaytostatesneartheedgesoftheirrespectivebands.Theexcessenergy is lost as heat and cannot be converted into usefulelectric power. Moreover, this heat decreases the PV cellefficiencyduetothermalgenerationofintrinsicchargecarriers[14].
Each metal island embedded within the depletion zoneforms a Schottky diode with the emitter part of the solarcell,ifthemetalwasselectedinaccordancewiththerelation(1). A current across this diode is defined by three distinctlydifferentmechanisms:diffusionofcarriersfromthesemicon-ductor into the metal, thermionic emission of carriers acrosstheSchottkybarrier,andquantum-mechanicaltunnelingthrough the barrier [17]. Such as our diodes are positionedin the external electrical field, generated by the built-inpotential of the photovoltaic diode, the thermionic emissionmechanism only defines current in these diodes. As known,the thermionic theory assumes that electrons with energylargerthanthetopofaSchottkybarrierwillcrossit.The

□=□□ln 2 , (3)

□

thermionicemissioncurrentisproportional tothesquare ofthejunctiontemperature,andthecurrentdensitycanbe

where□□=□□/□isthethermalvoltage,□istheBoltzmann'sconstant,Tistheabsoluletemperatureoftheenvironment

expressedinthefollowingform:

inK,□istheelectron'scharge,□□and□□aretheimpurity

=□*□^{2}exp(−□□)(exp(□□)−1), (6)

concentrationsinthebaseandtheemitter,respectively,and□□

□□

□□

istheequilibriumintrinsicconcentrationofchargecarriers.

where□isthedirectvoltageappliedtothediode,inourcase Thisvoltageproducesasufficientelectricalfieldtoprovide

□ *

separationofallchargecarrierswithinthedepletionregion.

□□=□□,A

istheRichardson'sconstant

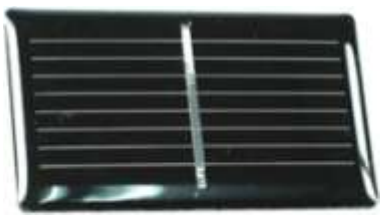
Duetosunlightirradiation,additionalchargecarriersaregeneratedinthisstructureandproduceelectricity.Efficiencyofsuchconventionalb PVcellisdefinedbytheincidentpower

$$\square^{*} = \frac{4\square\square\square^{*}\square^{2}}{h^{3}}$$

,(7)

TABLe 1:Parametersof thestandardPV cellofSZGD6030type [19].

Monocrystalline blacksolarcell
Efficiency: 15%Peakvoltage($□_{mp}$): 0.48V
Opencircuitvoltage($□_{oc}$):0.55V
Peak current ($□_{mp}$):280mA
Shortcircuitcurrent($□_{sc}$):302mA
Dimensions:60× 30× 2.8mm



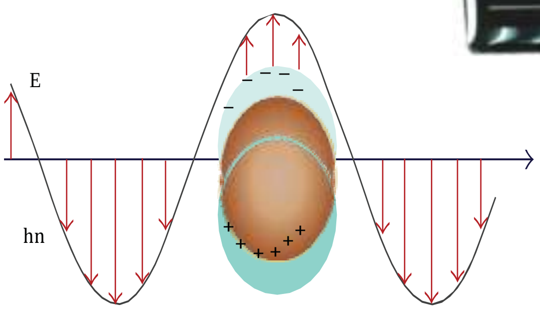


FIgURe4:ExcitationoftheSPRinthegoldisland[18].

where□=19.3 g/cm^{3}isthedensityofthegold,□=197 g/mole is the atomic weight of the gold, and □= 6.02 $\cdot 10^{23}$1/mole is the Avogadro’s number. An average volume ofoneislandis

and□*istheeffectivemassoftheelectroninthesemicon-

0^2

$□ = h \cdot □_4$

$1.5 \cdot □ \cdot 20^2 \cdot 10^{-21}$

=

4

$= 4.7 \cdot 10^{-19}$ cm^3.

(11)
ductor.
Fulladditioncurrentwhichshouldbeobtaineddueto
Therefore, an average number of free electrons in the islandwillbe
insertingthemetalislandfilmintothePVjunctionmaybe

□=□·□=$2.8\cdot10^{4}$electrons. (12)
estimatedasasumofcurrentsintroducedbyeachislandin
e □ □
thefollowingway:
□

$□_{ad}$=□∑□□□□, (8)
Anaveragenumberofislandspersurfaceunitareaindefinedconditions[11]is

□= 30 / $10^{4}\cdot10^{-14}$ = $3\cdot10^{11}cm^{-2}$
(13)
where□□□isthecurrentfromthemetalisland,□isanindex,

□isanaveragenumberofmetalislandsperunitarea,□□
isanaveragecontactsurfaceareabetweenthemetal'sisland
and emitter, and A is the active surface area of the PV cell.Therefore,themaximumgeneratedcurrent(seerelation(5))willtakethefollowingform:
Thus, if we assume that all free electrons from all islandswill participate in the conductance process, we obtain theadditionalelectroncurrentdensity,whichwillbeequalto

$□_{ad}$=□□e□=$3\cdot10^{11}\cdot2.8\cdot10^{4}\cdot1.6\cdot10^{-19}$

$□_m$=(□+□)(□□ □ ad □ m −1). (9)

=$1.4\cdot10^{-3}$
A/cm^{-2}.
(14)

DISCUSSION

For a quality assessment of the influence of the metal islandinterlayer, imbedded within the PV junction, on the cell'sefficiency,wetakeastandardPVcell.Thecell'sparametersare shown in Table 1. Evidently, the exact parameters of thecellarenotopened;however,itisknownthattheusedsiliconwas grown by the Czochralski method, and the missingparametersmaybetakenfrom[18].

Parameters of the gold island film were taken from theexperimental work [11], in which the number and size ofgold particles wereevaluated using AFM microscopy. Tobespecific,wechoseforourevaluationagoldfilmwithanaveragethicknessofh=1.5nm.Anaveragediameterof

the island equals approximately to 0= 20 nm. An averagenumber of islands is∼30 on an area of 100 × 100 nm. Now,wecanestimateanumberoffreeelectronsexistinginthe islandusingassumptionthateachgoldatomcontributesoneelectron to the conductive band. The number of gold atomsintheunitofvolumeisequalto

Due to excitation of SPR in the gold islands under lightirradiation, also holes come into resonance and create thecorrespondingcurrent,asshowninFigure4[18].So,gettingadditionalcurrentmustbedoubled.

Therefore, the total resulting current obtained from aconventional PV cell [19] with imbedded thin gold island filmbetweenbaseandemitterwillbeequalto

$□_{ad}$= 2$□_{ad}$□ = $2\cdot1.4\cdot10^{-3}\cdot6\cdot3$ = 50.4 mA.(15)CalculationofefficiencyofthenovelPVcellwith(5)and

(4) shows an increase in efficiency of 17% and gives 17.5%instead 15% without the gold film. This result agrees well withthe experimental data [20] where efficiency of organic solarcells, based on the bulk heterojunction system with silvernanoparticles,wasincreasedby17%aswell.

CONCLUSION

In this paper, we investigated the possibility to increase thesolarcellefficiencythroughintroductionofgoldislandfilm

□=

□ ___

□

□=

$$\frac{19.3}{197} \cdot 6.02 \cdot 10^{23} = 5.9 \cdot 10^{22} \text{cm}^{-3}, \quad (10)$$

between the emitter and base of a silicon semiconductordiode structure. We showed that the gold islands createa setof elementarySchottkydiodes.Thesediodes areinforward

bias condition due to its built-in electrical field within theemitter-basediodestructure.TheseSchottkydiodescaninject the free electrons, excited by sunlight irradiation, inthe conduction band of the semiconductor, and by this wayincreasethemaximumcurrentgeneratedbythesolarcell. Tentativecalculationdoneonastandardsolarcellshowedanincreaseintheefficiencyof17.5%.Thisresultisingoodagreementwithexperiments.

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