A New Strategy for Efficient Solar Energy Conversion: Parallel-Processing With Surface Plasmons

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A NEW STRATEGY FOR EFFICIENT SOLAR ENERGY CONVERSION:

PARALLEL-PROCESSING WITH SURFACE PLASMONS

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ABSTRACT

This paper introduces an advanced concept for direct conversion of sunlight to electricity, which aims at high efficiency by tailoring the conversion process to separate energy bands within the broad solar spectrum. The objective is to obtain a high level of spectrum-splitting without sequential losses or unique materials for each frequency band. In this concept, sunlight excites a spectrum of surface plasma waves which are processed in parallel on the same metal film. The surface plasmons transport energy to an array of metal-barrier-semiconductor diodes, where energy is extracted by inelastic tunneling. Diodes are tuned to different frequency bands by selecting the operating voltage and geometry, but all diodes share the same materials.

SYNOPSIS

Surface plasmons (refs. 1 and 2) are guided electromagnetic waves, which can be supported on thin films of common metals, like aluminum or silver. Thicker substrates may also be used, and there may be native oxides or dielectric overlayers. The surface plasma wave (fig. 1) consists of a propagating wave of surface charge (polarized valence electrons) accompanied by transverse and longitudinal electromagnetic fields which decay exponentially with distance from the metal interface. Typically, the fields extend a tenth to several thousand microns above the metal, but only penetrate a few hundred angstroms into the substrate, permitting integration with back surface diodes. This also allows an extremely lightweight system for space use, or a materials-conservative device on a low-cost substrate for terrestrial applications. The surface plasmon spectrum is broad and continuous from the infrared to cut-offs which lie in the visible or ultraviolet depending on material. The velocities are relativistic except near cut-off. Of course, for broadband energy transport, we are primarily interested in the relativistic waves, rather than the better known quasistatic ones.

The relativistic waves have field patterns in which most of the energy travels just above the metal. This feature reduces the effects of substrate absorption (ref. 2). Compared with the 3 to 5 micron range of conduction electrons in a GaAs solar cell, the surface plasmon range is excellent - typically, 75 to 5000 microns at solar frequencies and centimeters in the infrared (ref. 3). The surface plasmon range does not place a severe constraint on the proximity of collecting diodes. In fact, the high values allow us to compromise materials quality, e.g. using evaporated films. This situation contrasts markedly with conventional solar cell design, where high purity single crystals are generally required to insure adequate electron and hole diffusion lengths.
There are three steps in the energy conversion process (fig. 2):

1. Sunlight excites surface plasmons when its fluctuating electric fields polarize surface charge on the metal. Coherent light is not required, but a prism, grating, or textured surface must be used to provide phase-matching between photons and slightly slower surface plasmons of the same energy.

2. The surface plasmons transport energy to an array of tunnel diodes, tuned to extract maximum power from waves in a different frequency bands. Diodes differ in geometry and operating voltage, but all share the same materials. The simplest type is an MIS diode formed from the conducting substrate, its native oxide, and a buried or front surface semiconductor electrode.

3. Energy is extracted by inelastic tunneling, a one-step process in which an electron from the low voltage (semiconductor) electrode simultaneously absorbs a surface plasmon and tunnels to higher potential in the metal. Ideally, the semiconductor bandgap prevents backflow by eliminating unwanted final state energy levels. In a circuit, the tunneling current and load resistance supply the operating voltage. Current flows in the power quadrant as inelastic tunneling raises electrons to higher potential, enabling them to do work on the load.

Surface plasmons have strong coupling to both light and tunneling electrons, although not yet in the same structure. With prism-couplers, for example, 99 percent conversion of monochromatic, p-polarized light to surface plasmons has been demonstrated experimentally on a variety of substrates (ref. 4). While in Al-Al₂O₃-Ag light-emitting diodes (ref. 5), tunneling electrons have a very high (order one) probability to excite slower junction plasmons which propagate along the metal/oxide interfaces (ref. 6). Coupling the surface plasmons to junction plasmons or guiding surface plasmons into the tunnels is a primary challenge in the design. Other barrier problems, such as backflow and coupling of broadband unpolarized light, are also being addressed in a long-range, high-risk program.

INTRODUCTION

Problem: The Broad Solar Spectrum

The primary barrier to efficient solar energy conversion (ref. 7) has been the broad solar spectrum, which extends from 0.4 electron volts in the IR to 3.5 eVs in the UV. In a silicon solar cell, sunlight is absorbed to produce monoenergetic (1.1 eV) conduction electrons which transport their excitation energy to a collecting junction. This mismatch wastes 56 percent of the incident power. More energetic photons can excite valence electrons into higher energy levels in the unfilled conduction band (fig. 3), however, hot electrons give up their excess energy (1.1 eV) to lattice vibrations in picoseconds before the electrons have traveled more than a few hundred angstroms. Thirty-two percent of the incident power is lost to heat as hot electrons relax to a relatively stable position at the bottom of the conduction band. Further phonon emission is prevented by the 1.1 eV gap in electronic energy levels; however, the semiconductor's bandgap also prevents absorption of low energy photons which carry 24 percent of the incident power. The efficiency can only be raised a few percentage points by using a different semiconductor to optimize this trade-off.
These fundamental losses are beyond the control of the solar cell designer, who considers events on a longer (microsecond) time scale. Now monoenergetic, the conduction electrons diffuse through the cell transporting the remaining 44 percent of incident power to the collecting junction where about half this energy is converted to electrical power. Subtracting a few percent for practical losses, like optical reflection, electrical resistance, and incomplete carrier collection, the best silicon cell efficiencies are under 18 percent for the AMO or outer space spectrum. After 28 years of solar cell development, the short circuit current approaches the theoretical limit calculated for realistic materials parameters, and the open circuit voltage is within 90 percent of this value, but few advanced concepts have emerged to overcome the fundamental losses associated with the broad solar spectrum.

Strategy: Parallel-Processing

Spectrum-splitting is the leading contender in advanced concepts for higher efficiency. Two sequential approaches have emerged, which provide a contrast to spectrum-splitting in a parallel-processor. In spectrophotovoltaic systems, the optical beam is split with dichroic mirrors and directed onto two or three different types of solar cells. In cascades, the cells are grown in a monolithic stack to allow transmission of low energy photons into lower bandgap materials; typically, the cells are made from lattice-matched III-V alloys, with heavily-doped tunnel junctions to interconnect them in electrical series. In both systems, the increased complexity and additive losses (like tunnel junction resistance) offset incremental efficiency gains after two or three cells, limiting the potential efficiency to about 30 percent AMO. Our objective is to obtain a higher level of spectrum-splitting without sequential losses or unique materials for each frequency band.

Parallel-processing has been the preferred route for increasing the number of frequency channels, however, the missing ingredient has been the identification of a broadband carrier with suitable range for energy transport. In the search for long-lived excited states, little attention has been paid to less stable, but relativistic waves, like the surface plasmon. Perhaps these collective modes were overlooked because their properties are unfamiliar, or more likely, they were ruled out due to a prevalent misconception that wave approaches are unsuited for incoherent light. In any case, surface plasmon properties seem ideal for broadband energy transport. Two questions remain: how to couple sunlight into the waves, and how to extract power to do work on a load.

COUPLING TO SUNLIGHT

General Principles

Sunlight can excite surface plasmons when fluctuating solar fields polarize surface charge on a conductor. S-polarized photons, which have purely tangential electric fields, can not induce charge on a smooth surface, but "deep" surface texture, on the scale of the wavelength, allows effective coupling of both polarizations (ref. 8).

Given charge fluctuations at a surface plasmon frequency, the collective response can not be excited unless parallel momentum is also conserved. Two primary techniques are used to phase-match photons to slightly slower surface plasmons of the same energy:
A slow-wave structure, such as diffraction grating (ref. 9), creates photon harmonics with parallel momentum shifted by multiples of the inverse period. When one diffracted order satisfies the phase-matching condition, energy is withdrawn from all orders proportionately. A rough or discontinuous surface (refs. 10 and 11) acts like a superposition of gratings, allowing phase-matching over a broad frequency range.

Alternatively, photons may be slowed by a medium of high refractive index. In a prism-coupler (ref. 12), phase-matching occurs at specific incidence angles which typically vary a few degrees across the solar band.

The excitation process preserves coherence, but does not require it; coupling between an incident photon and surface wave can be calculated classically from Maxwell's equations. Figure 4 shows Otto's method of attenuated total reflection (ref. 12): generally, the surface wave component is small and almost all the light is reflected out of the prism. A strong dip in the reflected p-polarized light with a resonant increase in the surface wave amplitude occurs for phase-matching between prism photons and surface plasmons on the metal/airgap interface.

Optical Systems

Since the surface plasmon velocity varies with frequency, a range of grating periods or prism incidence angles is required to couple the solar spectrum. One strategy shown in figure 5 would use a prism or lens to disperse the spectrum over a fixed grating near parallel incidence. Angular dispersion controls the effective grating period and directs the surface plasmons towards appropriately-tuned diodes on the front surface. This resembles the IR sensor spectrum analyzer (ref. 13), a centimeter-size chip using a waveguide geodesic lens to disperse Bragg-scattered laser light to one of a hundred photodetector elements. Due to the required collimation and focusing optics, a guided wave approach appears most compatible with miniature concentrators - like TRW's penny-sized 100x Cassegrainian (ref. 14).

The requisite grating period depends on incidence angles, and geometry. At oblique incidence, visible wavelengths are normally required. For pure parallel incidence, the grating supplies only the small momentum mismatch, so periods must be longer (up to a centimeter) and become unduly sensitive to oxides and collimation. Fortunately, perfect collimation and phasematching are not required as any structure has built-in momentum uncertainty, inversely proportional to the parallel dimension.

Alternatively, natural sunlight with a range of incidence angles could be coupled to surface plasmons on a textured surface. This has the virtue of simplicity and potential low-cost for large-area systems without concentration or tracking. Since waves of different frequencies are co-excited without preferred direction, the collecting diodes should respond to specific frequency bands. This may prove possible in double-barrier (ref. 15) or superlattice (ref. 16) diodes which have tunneling resonances due to interference of the electron wavefunctions (ref. 17). Or we could use sequential absorption, beginning with the high energy plasmons which also have the shortest range.
Coupling Efficiency

Coupling to surface plasmons is resonant and can be virtually complete in phase-matched structures. As early as 1902, Wood observed anomalies in the scattered light from gratings, (refs. 9 and 18) which Lord Rayleigh explained as diffraction into a pair of superficial waves, (ref. 19) later termed a surface plasmon. In 1941, Fano first explained the anomalously large amplitude of the surface wave with an analogy to resonances in a mechanical system (ref. 20). With prism-couplers, 99 percent conversion of monochromatic, p-polarized light to surface plasmons has been demonstrated experimentally on a variety of substrates (ref. 4). References 21 and 22 show experimental evidence for strong (80 percent) coupling on unoptimized gratings and rough surfaces respectively.

The discovery of the giant Raman effect has intensified research on surface plasmon excitation (ref. 23). When some molecules are absorbed on a roughened metal surface, the measured Raman scattering cross-section can be up to ten million times larger than for the same molecule in solution (ref. 24). Controversy over the theory continues (ref. 25), but a common theme involves classical field enhancement due to the surface plasmon resonance (ref. 26).

Conclusions

Coupling sunlight to surface plasmons poses unique design problems since the light is unpolarized, uncollimated and broadband. However, the principles of resonant coupling with prisms, gratings, or textured surfaces are known, and high efficiencies can be expected. For a concentrator system, the uncertainties lie in the trade-off between quality optics and low cost. Rough surface coupling is more speculative, particularly regarding frequency-selective diodes. Research at the University of California at Irvine will evaluate coupling efficiency and scattering from deeply textured surfaces.

Energy Extraction by Inelastic Tunneling

Surface plasmons transport energy to an array of tunnel diodes tuned to extract maximum power from waves in different frequency bands. Although the diodes differ in geometry and operating voltage, all share the same materials. The simplest tunnel diode would be a metal-barrier-semiconductor junction formed from the conducting substrate, its native oxide, and a buried or front surface semiconductor electrode. The metal and semiconductor are at different potentials with the oxide serving as a barrier to inhibit electron flow.

Energy is extracted from the surface plasmons by inelastic tunneling, (refs. 6 and 27) a one-step process in which an electron from the low voltage (semiconductor) electrode simultaneously absorbs a surface plasmon and tunnels to higher potential in the metal. The semiconductor is doped heavily $p^+$, so its Fermi level lies close to the valence band. Almost all the energy can be extracted from surface plasmons with energy slightly more than the operating voltage. The surface plasmon excites an electron from the semiconductor valence band into an empty state just above the metal Fermi level, where there is little excess to be lost to heat.

Ideally, the semiconductor bandgap prevents backflow by eliminating the final state energy levels which could otherwise be reached by conventional
elastic tunneling (ref. 28) or by inelastic tunneling with emission of surface plasmons whose energy is less than the operating voltage. Some backflow through surface states and defects is unavoidable.

In a steady-state circuit, load resistance times the net tunneling current results in the impressed voltage across the diode. Current flows in the power quadrant as inelastic tunneling raises electrons to higher potential enabling them to do work on the load. Since the diode voltage determines the fraction of surface plasmon energy extracted, the load should be regulated to maintain constant voltage as the current varies with solar flux.

**Precedent: Tunable Light-Emitting Diodes**

In 1976, Lambe and McCarthy of Ford Motor Co. (ref. 5) first demonstrated tunable light-emitting diodes based on the LEIT effect: light emission by inelastic tunneling (refs. 29 and 30). As shown in Fig. 7, a voltage is applied across an MOM junction to cause inelastic tunneling with emission of surface or junction plasmons. These waves can radiate if the surface is roughened to provide phase-matching. When the voltage is varied from 2 to 4 volts, the color changes from red through blue-white with uniform glow across the outer electrode surface. Although still extremely inefficient, these are room temperature, reasonably stable devices of relatively large (mm$^2$) area.

In present LEDs, the glow can only be seen in a dark room - implying efficiencies less than $10^{-5}$ percent. What went wrong? As shown in figure 8, the applied voltage causes a current of tunneling electrons which have a very high (order one) probability to excite slow junction plasmons which propagate along the tunnel interfaces (ref. 6). Unfortunately, junction plasmons are absorbed by the substrate before they can radiate through the silver electrode. Five orders of magnitude difference in the mean free paths for substrate absorption and radiation seems to explain the low efficiency (ref. 6). When LEIT diodes are grown on visible frequency holographic gratings, a technique demonstrated in 1980 by Kirtley, Theis and Tsang of IBM (ref. 31), the plasmons are emitted on the outer electrode surface where they can radiate effectively. This time the efficiency is low (again $10^{-5}$ percent) due to weak coupling to the tunneling electrons (ref. 32).

**Outlook**

In the NASA program, we are trying to use surface plasmons for efficient coupling to light, and junction plasmons for coupling to tunneling electrons. Coupling the surface plasmons to junction plasmons is a primary challenge in the design. An obvious solution would be to thin the top electrode, so solar fields could penetrate into buried junctions. Improving the overlap may not be good enough, since the surface and junction plasmons hybridize with most of the energy still traveling above the metal/air interface.

A Berkeley grant is exploring the use of tapers to guide surface plasmons into tunnels on the front surface. The situation is easier for photodiodes than it is for LEDs, since the controlling mean free paths are different. Surface plasmons can be efficiently excited by light. Their long range leaves room to design graduated structures which shift fields into the tunnels. Junction plasmons have shorter range, typically a few microns, but preliminary calculations from Berkeley suggest a comparable range for junction plasmon
capture by tunneling electrons. This would be a good starting point for efficient diodes, however, quite a bit more theoretical modeling and experimental characterization is necessary before we are confident of our understanding of processes occurring in the tunnel diodes.

Another approach may be to phase-match surface waves to bulk modes. Coupling between surface plasmons and molecular excitons is discussed in reference 33 as a technique for transferring energy into dye molecules on the lower surface of a prism-coupler. Experiments on an analogous surface acoustic wave system have demonstrated nearly 100 percent transfer of surface waves from upper to lower surfaces of a thick LiNbO3 slab using gratings to phase-match the SAWs to bulk plate modes (ref. 34).

Further research is also required to determine the feasibility of energy extraction by inelastic tunneling. The issues are now well inelastic tunneling competes with substrate absorption as a mechanism for junction plasmon capture, and how much backflow limits the current.

CLOSING REMARKS

This paper has introduced a new strategy for efficiency solar energy conversion based on parallel-processing with surface plasmons. The approach is unique in identifying: (1) a broadband carrier with suitable range for energy transport, and (2) a technique to extract more energy from the more energetic photons, without sequential losses or unique materials for each frequency, band. The aim is to overcome the fundamental losses (50 percent) associated with the broad solar spectrum, and to achieve a higher level of spectrum-splitting than has been possible in semiconductor systems.

Surface plasmons should lend themselves to an exciting new class of electro-optic devices, operating over a broad frequency range in the IR through UV. The waves can be supported on common metals, like aluminum or silver, with only a thin film required. This allows extremely lightweight systems for space use, or materials-conservative devices on low-cost substrates for terrestrial applications. The long surface plasmon range allows some compromise on materials quality, and leaves room to design graduated structures which shift fields into the tunneling region. Surface plasmons have strong coupling to both light and tunneling electrons; the challenge will be to accomplish both in the same device.

REFERENCES


19. Lord Rayleigh, Phil. Mag. 14, 60 (1907).


Figure 1. Surface plasma waves.

Figure 2. Parallel processing with surface plasma waves.
Figure 3. - Solar cell losses.

Figure 4. - Prism-coupler resonance.
Figure 5. - Coupling to sunlight.

Figure 6. - Extracting power from surface plasmons.
INPUT: 2-4 VOLTS
OUTPUT: RED-BLUE/WHITE LIGHT

SURFACE PLASMONS

200 Å SILVER
20-40 Å NATIVE OXIDE

TUNNELING ELECTRONS

ALUMINUM FILM

JUNCTION PLASMONS

LIGHT

Figure 7. - Tunable light-emitting diodes.

EFFICIENCY: 10⁻² % BY EITHER PATH
(DIODES GLOW IN A DARK ROOM)

Figure 8. - Energy flow in tunable LEDs.
CRITICAL TECHNOLOGY: SURFACE TO JUNCTION PLASMON TRANSFER
PRECEDENT: 99% TRANSFER DEMONSTRATED FOR SAWs

Figure 9. - Energy flow in photodiodes.
This paper introduces an advanced concept for direct conversion of sunlight to electricity, which aims at high efficiency by tailoring the conversion process to separate energy bands within the broad solar spectrum. The objective is to obtain a high level of spectrum-splitting without sequential losses or unique materials for each frequency band. In this concept, sunlight excites a spectrum of surface plasma waves which are processed in parallel on the same metal film. The surface plasmons transport energy to an array of metal-barrier-semiconductor diodes, where energy is extracted by inelastic tunneling. Diodes are tuned to different frequency bands by selecting the operating voltage and geometry, but all diodes share the same materials.