Superficies y Vacío 7, 1-5 (1997)

Amorphous silicon alloys -- the optoelectronic materials that set the trend for photovoltaic applications

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Optoelectronic properties of thin film amorphous silicon and silicon-germanium alloys will be reviewed. Solar cell performance for various device structures using these materials will be presented. World record stabilized efficiencies of 11.8% and 10.2% for active-area devices and one-square-foot modules, respectively, have been achieved using a spectrum-splitting structure. These records have been confirmed by the National Renewable Energy Laboratory.

The continuous roll-to-roll process has become the trend for the most efficient manufacturing technology. Large scale building-integrated photovoltaic applications are being demonstrated worldwide. The trend for photovoltaic applications is clearly steered toward using the advanced optoelectronic material of amorphous silicon alloys.

I. INTRODUCTION

As we continue to enjoy the rapidly advancing technology of the twentieth century, we must also prepare for the challenges of the twenty-first century. Energy will undoubtedly become a major issue if we do not urgently address its availability, its environmental impact, or its ecological consequences. As we continue to deplete the precious resources of the earth, we are also polluting the air, the water, and the soil. Human activity is altering the composition of the atmosphere in unprecedented ways. Fossil fuel combustion, in combination with deforestation, has increased atmospheric concentrations of carbon dioxide twenty-five percent above preindustrial levels [1]. Global warming, or the greenhouse effect, has become a serious concern [2]. In modern history, we have even witnessed international conflicts or wars due to energy crises. After the tragic explosion in Chernobyl in 1986, European countries have launched a major effort in searching for alternate energy sources. Solar energy, the most abundant, nondepletable, and environmentally safe energy, is once again seriously considered.

Photovoltaic, the phenomenon that converts the sunlight directly into electricity, was first demonstrated about one hundred and fifty years ago [3]. In 1941, the first crystalline silicon device was developed [4]. However, photovoltaic is still far from reaching the commercial level that one would like to achieve today, due mainly to the high cost of the product. Amorphous silicon photovoltaic, a thin-film technology, has emerged as a strong contender for achieving low-cost solar cells to meet the challenges of the twenty-first century.

In this paper, we will present data on various amorphous silicon alloy solar cell structures, including world record stabilized efficiencies of 11.8% and 10.2% for small-area devices [5] and large-area modules [6], respectively. We will also present the most advanced manufacturing technology using a continuous roll-to-roll process [7].

Thin-film photovoltaic is increasingly being used for rural electrification. Building-integrated standing-seam [8] and shingle design [9] products as an alternate energy source are expected to provide building architects a new design dimension. Public awareness of the dangers of burning fossil fuels as well as the technological innovations in thin-film photovoltaics have provided optoelectronic amorphous silicon alloy material a golden opportunity to play a major role in supplying clean energy in the twenty-first century.

II. MAJOR ADVANTAGES OF AMORPHOUS SILICON ALLOY SOLAR CELLS

Amorphous silicon alloy, a thin-film material with properties different from conventional crystalline material, offers a new perspective to the photovoltaic technology. The major advantages of amorphous silicon solar cells are listed below:

1. Silicon and hydrogen, the two important ingredients, are extremely abundant.
2. Amorphous silicon possesses high optical absorption coefficient ($> 10^5$ cm^{-1}) over most of the visible spectrum, making thin film (< 1 μm) devices possible and cost-effective.
3. Amorphous silicon is easily doped by boron and phosphorous for *p*-type and *n*-type materials, respectively.
4. The optical bandgap of the material can be varied between 1.1 eV and 2 Ev by alloying with germanium or carbon.
5. Deposition technique employs simple low temperatures (< 350 °C), and can be easily scaled up to large areas (> m^2).

6. High deposition rates can be obtained. Rates of up to 100 Å/s using microwave excitation have been demonstrated [10].
7. Stacked multijunction structures and cell interconnect can be made readily.

It can be easily seen that low-cost and high-efficiency solar cells are not only possible but also achievable. While the biggest challenge is to provide photovoltaic at a cost competitive with conventional fossil fuel or nuclear energy, one must also take into account the social and environmental penalty that one pays by not using the most fundamental form of energy from the sun.

III. OPTOELECTRONIC PROPERTIES OF AMORPHOUS SILICON ALLOY MATERIALS

Amorphous silicon films have been prepared by various techniques such as chemical vapor deposition (CVD), photo-CVD, hot wire, electron-cyclotron resonance (ECR), sputtering, evaporation, glow discharge of plasma-enhanced chemical vapor deposition (GD or PECVD), etc. Films produced by evaporation or sputtering generally possess too high a density of states (DOS) in the mobility gap to be useful in device applications. Films prepared from GD, on the other hand, resulted in low DOS as first demonstrated in the early 1970's. It was later discovered that these films contained approximately ten atomic percent hydrogen and were since then referred to as a-Si:H or hydrogenated amorphous silicon. Today, most laboratories use the glow discharge technique to prepare amorphous silicon alloy samples.

A glow discharge of a gas can be accomplished by applying either a dc or a rf electric field using either inductively coupled or capacitively coupled planar-type systems. The properties of a-Si:H films by GD depend on deposition conditions such as pressure of the gas, substrate temperature, applied dc or rf power, separation of the electrodes, etc. Typically, high quality films are obtained by using pressure of 100 mTorr to 1 Torr, substrate temperature of 200 °C to 350 °C, electrode separation of 2 cm to 5 cm, and power density of up to 100 mW per square centimeter.

Silane (SiH_4) or disilane (Si_2H_6) gas with H_2 dilution are commonly used in GD as the feedstock materials for a-Si:H films. The optical bandgap of these films is approximately 1.7 Ev. Madan, Ovshinsky, and Benn [11] reported that fluorinated amorphous silicon (a-Si:H:F), prepared from silicon tetrafluoride (SiF_4) and H_2 gas mixture, exhibited good optoelectronic properties. It was suggested that due to the higher electronegativity, fluorine acts as a better dangling bond terminator than hydrogen, thus better quality.

The feedstock for producing a-SiGe:H:(F) films includes silane, germane, disilane, silicon tetrafluoride, hydrogen, and germane tetrafluoride. The bandgap of the material can be varied between 1.1 Ev and 1.7 Ev depending basically on the amount of germanium incorporated in the film. The higher the germanium concentration, the lower the bandgap. High quality alloy material is usually obtained with less than 50% germanium in the film. For wide bandgap materials, silane and methane (CH_4) or silane and ethylene (C_2H_4) have been used to produce a-SiC:H films with bandgaps ranging from 1.8 Ev to 2.8 Ev. The quality of a-SiGe:H or a-SiC:H, as measured from various characterization techniques, is generally poorer than that of a-Si:H. Other alloy materials such as a-SiSn:H or a-SiN:H exhibited much poorer quality and received little attention.

The most intriguing phenomenon in a-Si:H is the so-called Staebler-Wronski (SW) effect [12]. It was reported that application of light can significantly affect the electronic properties of the material such as conductivity. However, the original properties can be restored upon annealing the sample typically at 150 °C for 30 minutes. There have been many investigations of photo-induced SW effects in a-Si:H films linked to material parameters. Changes have been observed in the carrier diffusion length [13], unpaired spin density [14], density of states in the gap [15], infrared transmission [16], and the movement of the Fermi level [17]. Recently, it was found that there is a correlation between the quality of the material and the microvoid density of the sample [18].

While a significant amount of experimental and theoretical effort has been directed toward the understanding of the Staebler-Wronski effect, the exact mechanism is still not fully understood [19,20]. Mechanisms such as the breaking of the weak Si-Si bond, hydrogen diffusion, impurities, or stress in the film have been proposed. It is clear that after light soaking, new defects are created in the bulk of the material and form recombination centers [21] that degrade the film quality. Despite these problems, the degradation phenomenon can be engineered out by improving the deposition methods and conditions, or in solar cell fabrications, using tandem structures.

IV. PERFORMANCE OF AMORPHOUS SILICON ALLOY SOLAR CELLS AND MODULES

There are basically two ways to deposit *p- i- n-*type devices. One is to deposit onto a top-conductive-oxide (TCO) coated glass superstrate with a p^+ layer, then followed by an intrinsic layer and an n^+ layer. A metal contact is deposited last to provide the second electrode, with the first electrode being the TCO as well as an antireflection coating. The second method is to deposit an n^+ layer onto a metal substrate followed by an intrinsic layer and a p^+ layer. A TCO is deposited last to provide as the second electrode and as an antireflection coating.

Several techniques have been developed to enhance the solar cell performance:

1. Light trapping technique: one uses a highly reflective textured metal and conductive oxide combination to provide light trapping within the device and enhance the photo-generated current.
2. Wide bandgap window layer material: one either uses boron doped microcrystalline p^+ layer [22] or a-SiC:H p^+ layer [23] to increase the bandgap and reduce the optical loss in the window layer.
3. Elimination or minimization of impurities from the system: one uses a load-lock system or separated-chamber system to minimize unintentional dopant incorporation or external impurities such as oxygen, carbon, or nitrogen.
4. Use of a novel bandgap profiling method in the a-SiGe:H cell for higher performance [24].
5. Multijunction structure: one incorporates wide bandgap cell on the top, mid bandgap cell in the middle, and low bandgap cell in the bottom to more efficiently utilize the incident solar spectrum [25].

The schematic diagram of a triple-junction structure is shown in Fig. 1. The top cell which captures the blue photons uses a-Si alloy with an optical gap of ~1.8 Ev for the intrinsic (*i*) layer. The *i* layer for the middle cell is a-SiGe alloy with about 20% Ge. The optical gap is ~1.6 eV which is ideally suited for capturing the green photons. The bottom cell captures the red and the infrared photons and uses an *i* layer of a-SiGe alloy with about 30-40% Ge corresponding to an optical gap of ~1.4 eV. Light that is not absorbed in the cells gets reflected from the Ag/ZnO back reflector which is usually textured to scatter the light at an angle to facilitate multiple internal reflections.

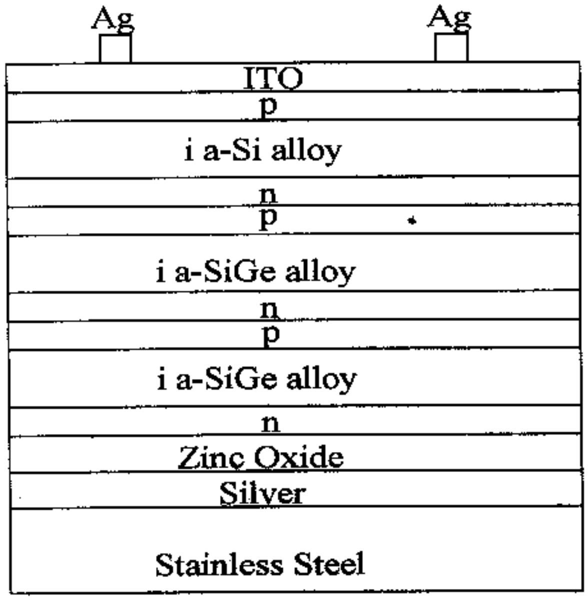

FIG. 1. Schematic diagram of a triple-junction structure.

Scientists at United Solar have achieved world record stable efficiencies of 11.8% for small-area cells [5] and 10.2% for large-area modules [6]. Table 1 lists solar cell performance for various device structures. These values are all world record efficiencies in their respective structures. Achieving 10% stable module efficiency using low-cost amorphous silicon alloy is considered to be a milestone for large-scale application of a-Si alloy solar modules.

TABLE 1. Highest stable cell efficiencies at United Solar for different junction configurations.

		J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	Deg.
a-Si:H	Initial	15.25	0.94	0.72	10.3	
	Degraded (600 hrs)	15.12	0.91	0.64	8.8	14.6%
a-Si:H/a-Si:H	Initial	7.9	1.89	0.76	11.4	
	Degraded (1000 hrs)	7.9	1.83	0.70	10.1	11.4%
a-Si:H/a-SiGe:H	Initial	10.67	1.65	0.72	12.6	
	Degraded (600 hrs)	10.61	1.61	0.66	11.2	11.1%
a-Si:H/a-SiGe:H/ a-SiGe:H	Initial	7.64	2.34	0.74	13.2	
	Degraded (1100 hrs)	7.49	2.28	0.69	11.8	10.5%

V. MANUFACTURING TECHNOLOGIES

There are basically two types of manufacturing technologies. One is to use a batch process and deposit single-junction or multijunction cells onto a glass superstrate. A laser scribing technique along with various in-line vacuum deposition and interconnect processes are employed. The "glass-in, panel-out" process [26] is limited by the size of the panel to a few square feet. The most attractive method is the roll-to-roll process [7] in which a roll of 2500-foot-long and one-foot-wide thin stainless steel is loaded for various steps of solar cell deposition. A novel gas gate design is used to avoid dopant diffusion. The advantage of this process is the continuous operation limited only by the length of the roll. The projected cost for a production volume greater than 75 MW per year is below $1 per peak watt. The manufacturers are not only striving to improve module efficiency, reduce manufacturing cost, and develop balance of system, they are also addressing issues such as module reliability and long-term stability. Warranties for ten years are being offered for power products.

VI. WORLDWIDE ACTIVITIES AND FUTURE PROSPECTS

Prior to 1984, amorphous silicon solar cells were basically used in consumer products such as calculators and watches. In 1984, several companies in the United States and Japan introduced the first amorphous silicon power modules of at least one square foot with power ratings of at least 5 watt. In 1986, several companies introduced 30-40 watt power modules. In 1989, Photovoltaic for Utility-Scale Applications (PVUSA), a cooperative project between the U.S. Department of Energy, the California Energy Commission, the Electric Power Research Institute, and several utility companies, started testing amorphous silicon modules with three 20 kW systems, setting the stage for amorphous silicon solar cells to enter the utility market for power generation.

Worldwide amorphous silicon shipments increased from 3.1 MW in 1983 to 13.7 MW in 1991. The worldwide amorphous silicon production capacity is expected to be 25 MW in 1997. This low-cost, thin-film technology is rapidly becoming a dominant force in the global PV market.

Until now, PV applications have been mostly for remote areas where PV is cost-effective as compared to diesel generators for uses such as irrigation and village lighting. Building-integrated photovoltaics, on the other hand, have recently been aggressively pursued and demonstrated. One example is the shingle design [9] that emulates asphalt shingles on the roof of an energy efficient house in Atlanta, Georgia. Another example is the standing-seam design [8] on the roof of a town house of the National Association of Home Builders. Public awareness of the environmental issues as well as the advances in thin-film photovoltaics make the outlook of the optoelectronic material of amorphous silicon alloys as bright as the sun.

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