a-Si:H Photodiode Using Alumina Thin Film Barrier

Chang-Wu Hur and Sima Dimitrijev, *Member, KIMICS*

Summary—A photodiode capable of obtaining a sufficient photo/ dark current ratio at both forward bias state and reverse bias state is proposed. The photodiode includes a glass substrate, an aluminum film formed as a lower electrode over the glass substrate, an alumina film formed as an insulator barrier over the aluminum film, a hydrogenated amorphous silicon film formed as a photo conduction layer over a portion of the alumina film, and a transparent conduction film formed as an upper electrode over the hydro-generated amorphous silicon film. A good quality alumina (Al_2O_3) film is formed by oxidation of aluminum film using electrolyte solution of succinic acid. Alumina is used as a potential barrier between amorphous silicon and aluminum. It controls dark-current restriction. In case of photodiodes made by changing the formation condition of alumina, we can obtain a stable dark current (~10^{-12}A) in alumina thickness below 1000Å. At the reverse bias state of the negative voltage in ITO (Indium Tin Oxide), the photo current has substantially constant value of 5×10^{-9}A at light scan of 100 lx. On the other hand, the photo/dark current ratios become higher at smaller thicknesses of the alumina film. Therefore, the alumina film is used as a thin insulator barrier, which is distinct from the conventional concept of forming the insulator barrier layer near the transparent conduction film. Also, the structure with the insulator thin barrier layer formed near the lower electrode, opposed to the ITO film, solves the interface problem of the ITO film because it provides an improved photo current/dark current ratio.

Key words—hydrogenated amorphous silicon film, photodiode, insulator barrier, alumina (Al_2O_3) film

I. INTRODUCTION

This paper proposes a photodiode exhibiting an increased on/off current ratio and a method for fabricating the proposed diode structure. To fabricate the photodiode, aluminum film is deposited in vacuum over a glass substrate. The aluminum film is formed by oxidation of alumina film using electrolyte solution of succinic acid. The aluminum/ alumina film is patterned by wet etching process to form the lower electrode and insulator barrier. Therefore, a hydrogenated amorphous silicon film (a-Si:H) is deposited to a thickness of 1μm over the entire exposed surface of the resulting structure. ITO film of transparent conductor is deposited over the a-Si:H film. Subsequently, the ITO film is partially etched. Using the etched ITO film as a mask, the a-Si:H film is patterned by use of the reactive ion etching (RIE) process.

Photodiodes have been used in facsimiles for sensing light, reflected from a document or other objects, and recognizing characteristics and letters. The accurate control of dark current is very important for gray scale level designation. If the level of dark current is imperfectly determined, the sensing operation is inaccurately achieved. Lots of photodiodes are used for a large document, including a white part at one portion and a black part at the other portion, so the characteristics of the photodiodes should be uniform. Material exhibiting appropriate energy gap should be used to obtain the accuracy in the sensing operation and the uniformity in device characteristic. Furthermore, the energy gap of this material must have a constant value to maintain the uniformity in device characteristic and control of the dark current. On the other hand, if the energy band gap is too large, it is impossible to accomplish the sensing function because all signals generated are detected as dark current. A large photo current can flow by controlling the flow of dark current and we can obtain a high I_{photo}/I_{dark} ratio. Therefore, good characteristics can be obtained in photodiodes with the insulator barrier layer of alumina film.

II. Al_2O_3 FORMATION BY ANODIZING METHOD

To form alumina, we have experimented with three electrolytes choosing succinic acid, ammonium tartrate, and boric acid when Al is anodizing. Testing was performed by 30mA, 60mA, and 90mA and voltages of 60V, 120V, and 180V in each electrolyte, respectively. The experimental conditions are listed in Table I. The experimental results have shown that the type of electrolyte didn't affect alumina thickness but affected the breakdown voltage. These results mean that the characteristics of alumina film depend on the type of electrolyte.

We could not measure breakdown voltage because it was very porous in case of boric acid. In the case of ammonium, the film was more sensitive, but the breakdown voltage was small compared to the succinic acid. Therefore, we experimented with succinic acid.

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Chang-Wo Hur is with Mokwon University (phone: 82-42-829-7655; fax: 82-42-829-7653; e-mail: chang@mokwon.ac.kr).

Sima Dimitrijev is with Mokwon University (phone: 82-42-829-7657; fax: 82-42-829-7653).

Table I. Conditions of alumina formation(anode oxidation)

Num.	Electrolyte	V_{limit} (V)	Current (A)	Thickness (Å)	(Å/V)	Breakdown Electric Field (MV/cm)
1	Succinic acid	60	30	800	13.3	6.25
2	Succinic acid	120	60	1800	15.0	6.67
3	Succinic acid	180	90	2600	14.4	6.15
4	Ammonium Tartrate	60	30	900	15.0	5.6
5	Ammonium Tartrate	120	60	1600	13.3	6.8
6	Ammonium Tartrate	180	90	2500	13.9	6.0
7	Boric acid	60	30	900	15.0	-
8	Boric acid	120	60	1700	14.2	-
9	Boric acid	180	90	2400	13.3	-

We have measured the breakdown characteristics of alumina film, formed under condition of succinic acid, and ammonium tartrate as electrolyte, respectively. We determined that succinic acid is superior to ammonium, the breakdown field of the alumina being 6.7MV/cm. Table 1 shows the parameters for forming alumina in the experiment. Figure 1 shows the change of thickness of Al_2O_3 film by anodizing power. Figure 2 shows the breakdown voltages of Al_2O_3 film as a separate test condition.

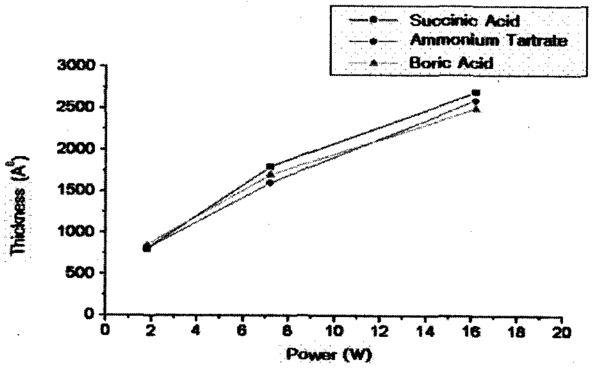
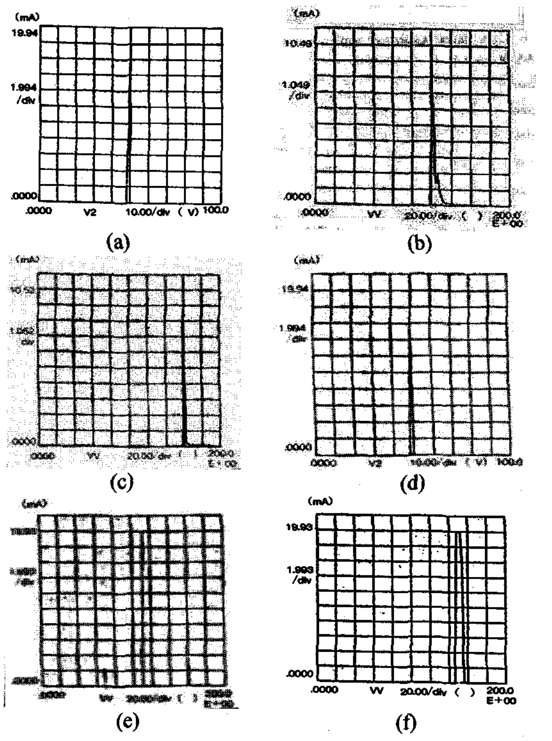


Fig. 1 Change of thickness of Al_2O_3 film by anodizing watts



(a) (b)

(c) (d)

(e) (f)

Fig. 2 Breakdown voltage of Al_2O_3 film

III. PHOTODIODE WITH A BARRIER OF Al_2O_3

Conventional amorphous silicon photodiode uses a Schottky contact with Cr/a-Si:H/ITO structure. Cr and a-Si:H have a quasi-Schottky characteristics and have a barrier height around 0.55eV. a-Si:H and ITO have characteristics with ~0.93eV barrier height. Because stoichiometry is not fully controlled by deposition of ITO, the Schottky contact is not fully formed at the amorphous surface, and the characteristics of the device show an unstable state. Many researchers have tried to create a stable Schottky characteristic in ITO and a-Si:H. Some researchers have focused on restriction of dark current by inserting an insulator layer near the interface of ITO and a-Si:H [1,2]. When the insulator layer is thick, the flow of dark current is restricted and we have to grow a film through which the photo current can tunnel. Shallow insulator formation (hundreds of angstroms) by using this method results in a film with pin-holes.

We propose a new idea to restrict the dark current using energy band so that the photo current can pass. We have realized that an insulator between Aluminum and a-Si:H can achieve a good result as above [3,4]. To get a high quality insulator, we choose the anodizing method and grew Al_2O_3 by anodizing the lower electrode of Al. This method can control easily the thickness and enable to realize excellent breakdown property. The experimental process is as follows.

First, glass substrate is cleaned, Al is deposited over glass substrate, testing the process with several conditions of anodization with succinic acid. Second, Al and Al_2O_3 are patterned and intrinsic a-Si:H deposited with a thickness of 1μm by PECVD (Plasma Enhanced Chemical Vapor Deposition). The flow rates of SiH_4 gas were varied between 40 and 150 sccm. The pressure variation of reactor is varied in the range from 0.2 to 0.8 torr. The substrate was maintained at the temperature of 250℃. The deposition rates of a-Si:H thin films were varied in the range from 120Å/min to 400Å/min. The optimum deposition conditions are listed in Table II. The a-Si:H thin films with the optimum deposition conditions have characteristics of optical bandgap of 1.7 eV, dark conductivity of ~10^{-10} S/cm and photo conductivity of ~10^{-7} S/cm respectively.

Table II. PECVD deposition condition of a-Si:H thin film

	SiH_4	Pressure	Temperature	Time	Rf Power	Thickness
Unit	sccm	torr	℃	min	W	Å
a-Si:H	40	0.4	250	60	30	9,600

ITO films show a low electrical resistance and high transmittance in the visible range of the optical spectrum. Therefore, they play an important role as transparent electrodes for current electronic devices. In this paper, deposition of ITO films on glass substrates was performed by the DC-magnetron sputtering system (HSD-662M: Cylindrical Type). The ITO target used for these experiments was a hot pressed In_2O_3 containing 10wt% SnO_2 made by Mitsui Mining Company. The distance between the target and substrates was about 80 mm. The deposition process was performed in a mixture of argon and oxygen gases where the gases were controlled by a mass flow meter. To control the electrical resistance and optical transmittance of the ITO films, various mixtures of the argon and oxygen were used as sputtering gases. Ar/O_2 was controlled in the range from 1.0 % to 15 %. The optimum O_2 content was 1.0 %. The ITO thin film deposited by the optimum O_2 content has good optical transmittance (90%) and low resistivity (300 μΩcm). The base pressure of the sputtering system was 9×10^{-7} torr, the process pressure was 5×10^{-3} torr and the sputtering power density applied in the process was 2.03W/cm^2. The film thickness was controlled by adjusting the deposition time to ~1500 Å. The deposition process was also accomplished at a relatively low temperature to reduce the thermal expansion of the aluminum thin film and annealing experiments were carried out using a conventional oven that has an air circulation facility or in the sputter chamber itself. Although the sputtering process was accomplished without an additional substrate heating, the temperature of the chamber rose up to 64-78 °C due to the plasma process. The substrate was annealed for 1 hour after its surface reached the set temperature. Moreover, in order to diminish the thermal expansion of the substrate and the deposited thin films, the temperature was slowly increased by stepped heating process. The optimum deposition conditions are listed in Table III.

Table III. Sputter condition of ITO thin film

	Ar	O_2	Temperature	Target	Power	Thickness
Unit	sccm	sccm	℃	(In_2O_3 : SnO_2)	W/㎠	Å
ITO	50	0.5	~70	90:10 wt%	2.03	1500

ITO, a-Si:H, and Al_2O_3 are patterned with RIE process at once. To reduce a damage by RIE, we have measured an electrode after annealing in air at 200~250℃ during 30 minute for 1hour. Figure 5 shows the energy band diagram of ITO/a-Si:H/Cr structure [5,6]. Figure 6 shows the energy band diagram of Al/Al_2O_3/i-a-Si:H/ITO structure in forward and reverse bias conditions. In forward bias, Cr and a-Si:H show quasi-Schottky contact. They exhibit large dark current because the dark current is not controlled properly. Therefore, significant photo current flows because of low barrier. By using forward bias, we cannot obtain a higher light/dark current ratio. In reverse bias, ITO has Schottky characteristics. Although a large photo current flows, the dark current is restricted by this barrier. Then, we can obtain a higher photo/dark current ratio. But, we have a problem in making the Schottky barrier because of unstable interface between ITO and a-Si:H in particular ITO stoichiometry [7]. Table IV shows the characteristics of a photodiode using Al_2O_3. Figure 3 shows the process flow and the structure of a photodiode with a barrier of alumina thin film.

Table IV.Characteristics of photodiode using Al_2O_3

Num.	Voltage (Volts)	Thickness (?)	Reverse bias			Forward bias		
			I_{off}(A)	I_{on}(A)	I_{on}/I_{off}	I_{off}(A)	I_{on}(A)	I_{on}/I_{off}
1	5	75	$5x10^{-13}$	$1x10^{-9}$	$2x10^3$	$6x10^{-12}$	$6x10^{-9}$	$6x10^3$
2	10	150	$9x10^{-13}$	$8x10^{-10}$	$8.9x10^2$	$5x10^{-13}$	$6x10^{-9}$	$1.2x10^4$
3	17	255	$8x10^{-13}$	$5x10^{-10}$	$6.3x10^2$	$1x10^{-12}$	$6x10^{-9}$	$6x10^3$
4	20	300	$8x10^{-13}$	$3x10^{-10}$	$3.8x10^2$	$2x10^{-12}$	$6x10^{-9}$	$3x10^3$
5	23	340	$1x10^{-12}$	$1x10^{-10}$	$1x10^2$	$5x10^{-13}$	$6x10^{-9}$	$1.2x10^4$
6	30	450	$7x10^{-13}$	$9x10^{-11}$	$1.3x10^2$	$6x10^{-13}$	$6x10^{-9}$	$1x10^4$

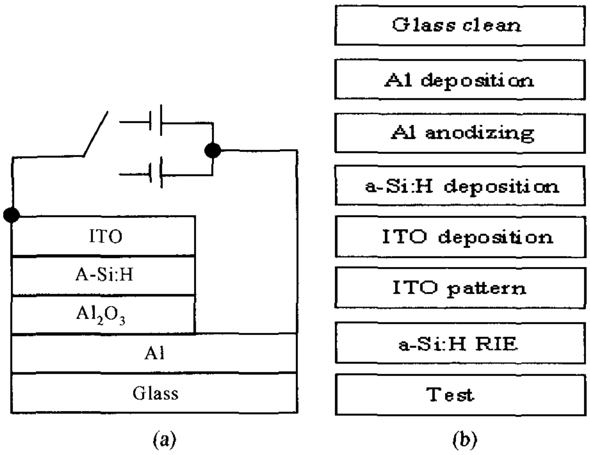


Fig. 3 Process flow and structure of photodiode with barrier of alumina

IV. ANALYSIS OF PHOTO/DARK CURRENT OF PHOTODIODE WITH Al/Al_2O_3/a-Si:H/ ITO STRUCTURE

A.

A. Negative voltage between Al and ITO : forward bias

In dark, Al_2O_3 takes the role of a potential barrier. It is restricted at its maximum value, which is below 10^{-12}A. When exposed to light, its barrier is changed according to thickness of Al_2O_3. That is to say, a smaller thickness of Al_2O_3 is formed, a higher current flows. As the thickness is large, the current is small. Figure 4 shows the photo/dark current of Al/Al_2O_3/a-Si:H/ITO structure as a test condition. As shown in Figure 4, we can estimate that generated photon is attracted by injected bias, electrons move toward ITO, and holes move toward Al direction. The barrier of Al_2O_3 does not affect the flow of electrons, however the flow of holes is affected by the barrier of Al_2O_3. The tunneling effect occurs when the barrier thickness of Al_2O_3 is below a critical value. In the case of charge generated by phonons, electrons can move easily, but holes are very sensitive to the thickness of Al_2O_3. In view of this phenomenon, we can estimate that the generation of photons in a-Si:H is restricted. The flow of holes is blocked and the photons generated in a-Si:H can be emitted outside as soon as electrons are generated. However, the holes are accumulated to compensate and electrons should be injected in to the alumina. This injected electrons have to tunnel through a dual barrier: a thin barrier of Al_2O_3 and Al/a-Si:H. As the thickness of Al_2O_3 is reduced, injection of electrons increases and the current increases. We can estimate that photon current in forward bias is sensitive and changes in proportion to the thickness of Al_2O_3 film.

B. Positive voltage between Al and ITO : reverse bias

In the case of photo, as Al_2O_3 is below the critical thickness, the thin barrier cannot prevent the current flow. But, in dark, Al_2O_3 serves as the current barrier. If thickness of Al_2O_3 is small, tunneling effect is enabled by the applied bias and dark current increases. From this point of view, we can obtain a higher photon/dark current ratio with around 1000 Å thickness after anodizing Al_2O_3. In this case, the dark current cannot tunnel through the Al_2O_3 plate. In its light, the generated photo carriers increase the Fermi level of a-Si:H of the interface between a-Si:H and Al_2O_3. We can estimate that this makes the tunneling possible. Figure 5 shows the energy band diagram of Cr/i-a-Si:H/ITO structure. Figure 6 shows the energy band diagram of Al/Al_2O_3/i-a-Si:H/ITO structure. Figure 7 shows that photo/dark current depends on the thickness of Al_2O_3 in the Al/Al_2O_3/a-Si:H/ITO structure.

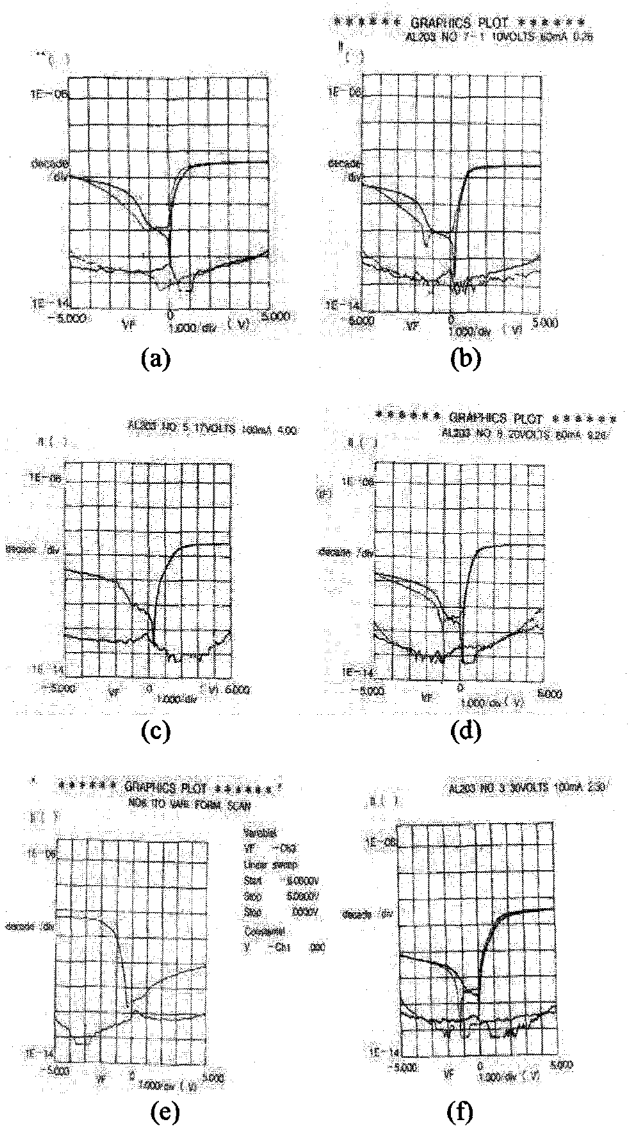


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Fig. 4 Photo/dark current of Al/Al_2O_3/a-Si:H/ITO structure (Test condition)

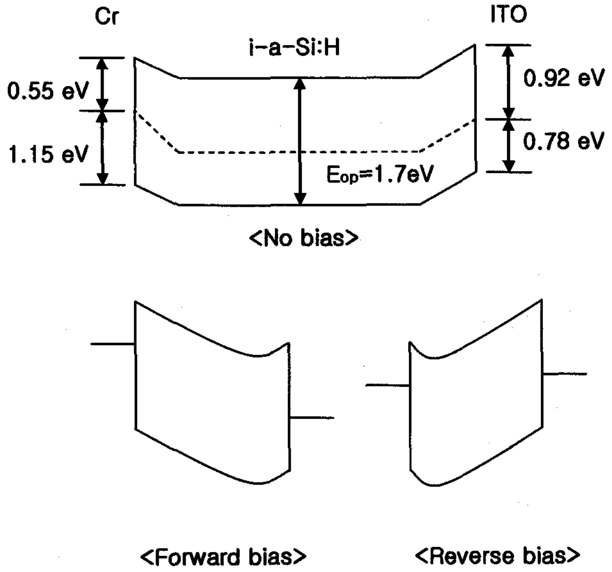

Fig. 5 Energy band diagram of Cr/i-a-Si:H/ITO structure

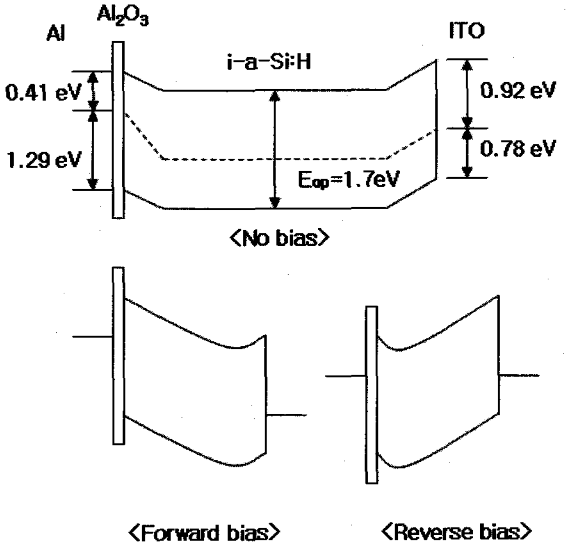

Fig. 6 Energy band diagram of Al/Al_2O_3/i-a-Si:H/ITO structure

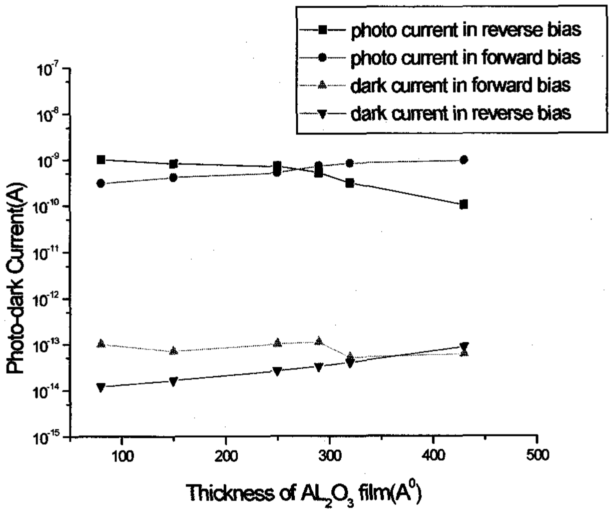

Fig. 7 Dependence of photo/dark current on thickness of Al_2O_3 in the Al/Al_2O_3/a-Si:H/ITO structure

V. CONCLUSION

A method to grow high quality Al_2O_3 film using anodizing technology and a new etching technique is proposed. From the experimental results, the photo current of photo diodes is large. On the contrary, dark current is very small at about 10^{-12}A. The photo current varies according to thickness of Al_2O_3 film. At the positive bias at Al and negative at ITO, the photo current is constant at 5×10^{-9}A. This shows that thickness of Al_2O_3 does not affect the photocurrent. Contrary to the conventional method [8], the proposed method provides a barrier at the opposite side of ITO. This approach can remove the problem of the interface of ITO. Therefore, we can estimate from the experimental results that a proper shallow barrier enables the good electrical characteristics.

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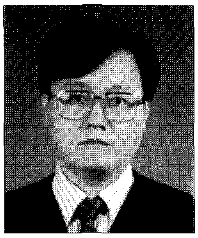
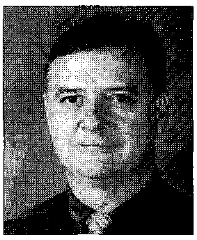


Change-Wu Hur
Received his B.S.degree in Electronic Engineering from Kwangwoon University in 1982 and M.S. and Ph.D. degrees in Electrical and Electronic Engineering from the Yonsei University in 1984 and 1991, respectively. From 1986 to 1994, he joined at LG Research Center, where he worked as Senior Member of Technical Staff. In 1994, he joined the department of Electronic and Information security Engineering, Mokwon University, Korea, where he is presently a associative professor. His research interest is in the area of VLSI and Display that includes ASIC design, Display technology and Wireless Communication design.



Sima Dimitrijev (S'87–M'88–SM'02)
Received the B.Eng., M.Sci., and Ph.D. degrees in Electronic Engineering from the University of Nis, Yugoslavia, in 1982, 1985, and 1989, respectively. From 1982 to 1983, he was with the Semiconductor Factory of the Electronics Industry, Nis, where he worked on the development of CMOS technology. From 1983 to 1990, he was with the Faculty of Electronic Engineering at the University of Nis. In 1990, he joined Griffith University, Brisbane, Australia, where he is currently a Professor at the School of Microelectronic Engineering. His current research interests are focused on SiC MOSFETs, including design, modeling, fabrication, characterization, and nonvolatile memory applications. He is the author of *Principles of Semiconductor Devices* (New York: Oxford University Press, 2006) and a member of the Editorial Board of *Microelectronics Reliability*.