

The Effects of Extended Heat Treatment on Ni Induced Lateral Crystallization of Amorphous Silicon Thin Films

Zhonghe Jin, Keith Moulding, Hoi S. Kwok, *Senior Member, IEEE*, and Man Wong, *Member, IEEE*

Abstract—The effects of extended heat treatment on the rate of metal induced lateral crystallization (MILC) of amorphous silicon (a -Si) were investigated. Orientation image microscopy and transmission electron microscopy were employed to reveal the crystallinity of the thin film and to measure the MILC length. It was found that for circular Ni disc patterns, the radial dimensions of the resulting MILC rings increased with the radii of the Ni discs. The longest MILC lengths were obtained from straight-edged Ni patterns, which effectively had infinite radii of curvature. The MILC rate decreased upon extended heat treatment. One reason is the continuously changing state of the a -Si during the treatment. An additional reason could be the diminishing supply of Ni from the Ni covered area. The contribution of both to the reduction of the MILC rate is discussed.

Index Terms—Lateral crystallization, low-temperature, nickel, thin film transistors.

I. INTRODUCTION

METAL induced crystallization (MIC) has been studied as a lower temperature alternative to solid-phase crystallization (SPC) of amorphous silicon (a -Si) [1]–[4] or amorphous SiGe [5] thin films. Recently, palladium (Pd) or nickel (Ni) [6], [7] was found to induce crystallization of a -Si outside its coverage area. This phenomenon of metal induced “lateral” crystallization, or MILC for short, has been found to produce polycrystalline silicon thin films largely free of metal contamination, with better crystallinity than those produced by SPC, and resulting in better performing thin film transistors [8], [9].

Having observed that in MILC by Pd, the rate changed inversely with the separation between the Pd pads, Lee *et al.* [6] proposed that the MILC rate depended on the local Pd concentration. We have recently observed that in MILC by Ni

Manuscript received March 6, 1998; revised October 1, 1998. This work was supported by a Competitive Earmarked Research Grant from the Research Grants Council of Hong Kong. The review of this paper was arranged by Editor C. Y. Yang.

Z. Jin was with the Department of Electrical and Electronic Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. He is now with the Department of Information Science and Electronic Engineering, Zhejiang University, Hangzhou 310027, China.

K. Moulding is with the Materials Characterization and Preparation Facility, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

H. S. Kwok and M. Wong are with the Department of Electrical and Electronic Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

Publisher Item Identifier S 0018-9383(99)00611-5.

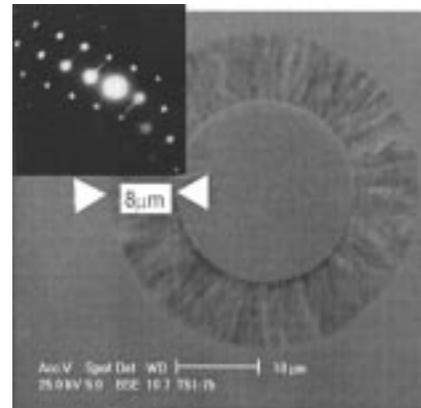


Fig. 1. Typical OIM micrograph of MILC induced by a 20 μm diameter Ni disc after 7 h of heat treatment at 500 $^{\circ}\text{C}$. Long, needle-like silicon grains are visible, forming a ring around the Ni disc. The Inset TED pattern indicates Si in the ring is crystallized with largely (110) planes parallel to the surface of the film.

[10], the rate decreased upon extended heat treatment. Clearly, the stability of the MILC rate is an important factor in device mass production. Therefore it is necessary to characterize the MILC rate and to understand its drift during extended heat treatment. This work concentrates on these aspects of MILC by Ni.

II. EXPERIMENTAL

The starting substrates were thermally oxidized, (100) oriented, 100-mm diameter silicon wafers. Thin 100 nm a -Si films were subsequently deposited by low-pressure chemical vapor deposition (LPCVD). Silane at a flow rate of 70 sccm was used as the Si source gas. The deposition pressure and temperature were 300 mTorr and 550 $^{\circ}\text{C}$, respectively. After the a -Si deposition, some of the wafers were capped by 100 nm of low temperature oxide (LTO) formed by LPCVD at 425 $^{\circ}\text{C}$.

A lift-off process using photoresist was employed to form patterned Ni on the wafers. The photoresist was first patterned to form the desired Ni features. For those samples with the LTO caps, the exposed oxide was removed in a buffered HF solution. For those without the LTO caps, an HF dip was employed to remove the native oxide on the exposed a -Si thin films immediately prior to loading into the Ni evaporator. The base pressure in the deposition chamber of the electron beam

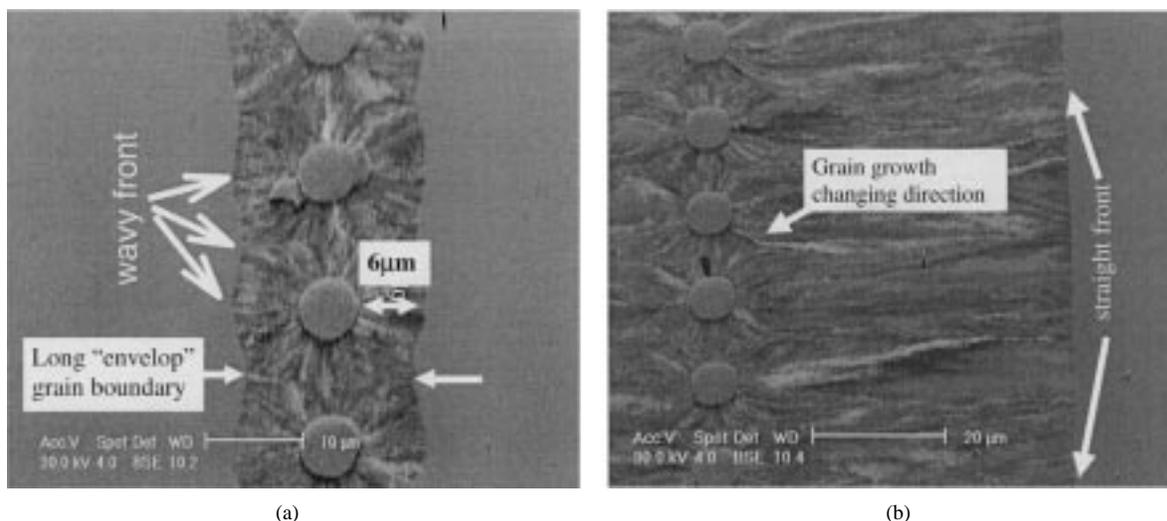


Fig. 2. MILC induced by a row of 5 μm diameter Ni discs after a) 7 and b) 48 h of heat treatments at 500 $^{\circ}\text{C}$.

evaporator was 10^{-8} Torr, but rose to 10^{-7} Torr during the evaporation. The wafers were cooled and their temperature kept below 100 $^{\circ}\text{C}$. Ni was deposited at a rate of about 0.02–0.03 nm/s. The total thickness deposited was about 5 nm and monitored by a quartz resonator. After the deposition, the wafers were dipped in acetone for over 10 h to dissolve the photoresist and to lift off unwanted Ni.

The effects of extended heat treatment on MILC rate were studied by pre-annealing a series of samples, including those with or without the LTO caps, for 70 h in N_2 at 500 $^{\circ}\text{C}$ before the Ni deposition.

After the Ni deposition, the wafers were cut into $1 \times 1 \text{ cm}^2$ square dies before the heat treatment at 500 $^{\circ}\text{C}$ for duration ranging from 1 to 70 h in a conventional atmospheric pressure, 6-in diameter horizontal quartz furnace. During the heat treatment, N_2 was delivered into the furnace at a rate of 5 L/min from a high purity liquid N_2 source.

Orientation image microscopy (OIM) using channeling contrast of back-scattered electrons was used to characterize the samples in a secondary electron microscope with an electron incident angle of 70 $^{\circ}$. Transmission electron diffraction (TED) was used to study the crystallinity of the polycrystalline silicon in the MILC region and secondary ion mass spectrometry (SIMS) was used for hydrogen content determination.

III. RESULTS

A typical OIM micrograph of a sample with a disc pattern and annealed for 7 h at 500 $^{\circ}\text{C}$ is displayed in Fig. 1. This sample did not have the LTO cap and had not been pre-annealed prior to the Ni deposition. A ring-like region is clearly visible around the disc. The TED pattern, taken in the ring and shown in the Inset of the figure, shows that the region is crystallized with a preferential (110) orientation. Micro-Raman scattering spectroscopy was also used to ascertain that the entire depth of the Si in the ring has been crystallized, thus indicating MILC has occurred in the ring. Long but narrow grains with widths on the order of 1–2 μm and lengths on the order of the radial dimensions of the MILC ring can be observed. The long axes

of these grains are perpendicular to the local edge of the Ni disc and the crystallization front is a uniform circle sharing the same center as the Ni disc. This shows that MILC is isotropic and that the grains grow in directions perpendicular to the local tangents on the crystallization front.

A series of closely spaced 5- μm diameter Ni discs was designed to study what takes place when the crystallization fronts from adjacent MILC regions “collide.” The resulting OIM micrographs are displayed in Fig. 2(a) and (b). After seven hours of heat treatment, the crystallization fronts from the neighboring Ni discs collided and formed distinct grain boundaries [Fig. 2(a)] at the center between any two adjacent Ni discs, with the entire series of Ni discs sandwiched between two long and wavy MILC fronts. After a total of 48 h of heat treatment, the wavy fronts straightened out as shown in Fig. 2(b). The long axes of the grains are again perpendicular to the local tangents on the new crystallization front, thus indicating that some of the colliding grains in Fig. 2(a) changed direction after the collision.

Fig. 3 shows the MILC induced by two Ni lines with different widths of 10 and 50 μm . Equal MILC lengths of 10 μm [Fig. 3(a)] were obtained next to both Ni lines after 7 h of heat treatment at 500 $^{\circ}\text{C}$. After a total of 48 h of heat treatment, the entire α -Si region between the Ni lines has been crystallized. A long and straight grain boundary dividing the original α -Si region into two halves is visible and highlighted by the arrows in Fig. 3(b). This indicates the MILC rates induced by the two Ni lines is the same, independent of their widths.

The MILC lengths and rates for the Ni disc and line are summarized in Fig. 4. The MILC rate is estimated by dividing the total MILC length by the total heat treatment time. For any given heat treatment time, both the MILC length and rate increase with the radius of curvature of the originating Ni pattern. Clearly the longest length and the fastest rate are obtained from a straight-line pattern, with its infinite radius of curvature. Yet regardless of the type of the Ni patterns, the MILC rates decrease upon extended heat treatment, consistent with previously reported observations [10].

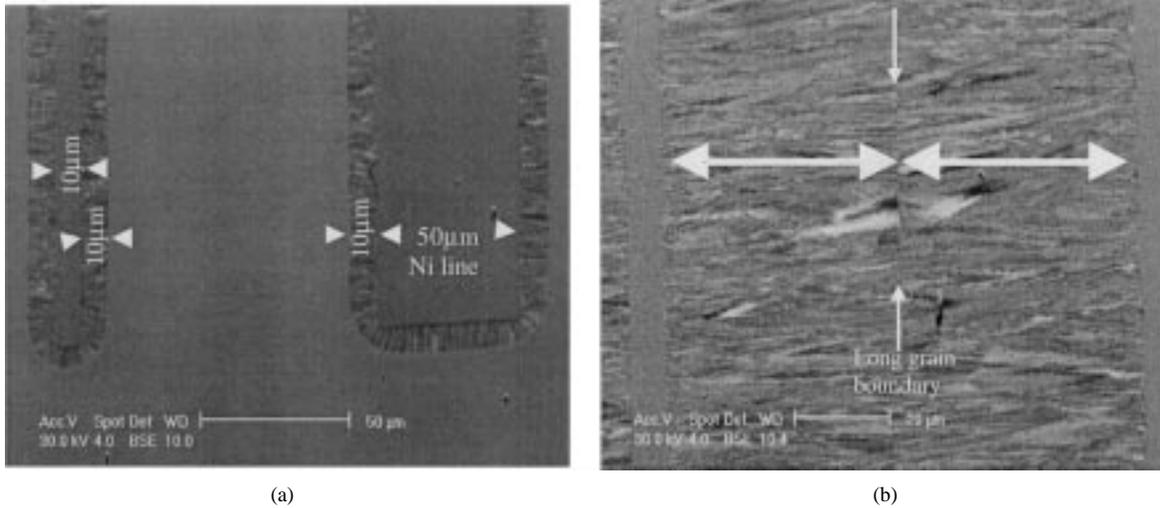


Fig. 3. MILC induced by straight Ni line patterns after (a) 7 and (b) 48 h of heat treatments at 500 °C. The widths of the lines are 10 and 50 μm , respectively. In (b), only part of the 50 μm wide Ni line can be seen on the right hand side of the figure.

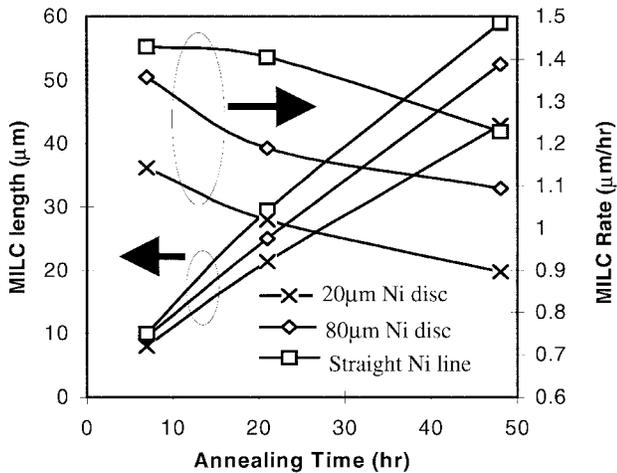


Fig. 4. The dependence of the MILC length and rate on the heat treatment time and the diameters of the Ni patterns.

The influence of the physical presence of the Ni covered area on MILC was studied using samples with the LTO coverage. After the Ni deposition, the samples were first heat treated for 3 h at 500 °C, resulting in the growth of a 4.8 μm wide MILC region. For some of the samples, any remaining Ni containing species in the area originally covered by the evaporated Ni was removed by first dissolving any metallic Ni in 40% HCl solution at 60 °C, followed by removal of the exposed Si and any silicides of Ni using plasma etching with a fluorine based chemistry. The etch rate of the Si film under the Ni coverage was found to be much slower than that of undoped Si, possibly due to the high concentration of Ni in the area. During the etching, the MILC region, together with any other area not originally covered by Ni, remained protected by the 100-nm-thick LTO layer. Both types of samples with and without the Ni removed were again subjected to extended heat treatments. The dependence of the MILC length and rate on the treatment time is summarized in Fig. 5. Clearly, the MILC lengths of the samples with the Ni removed show a stronger tendency to “saturate” and the corresponding MILC rates are

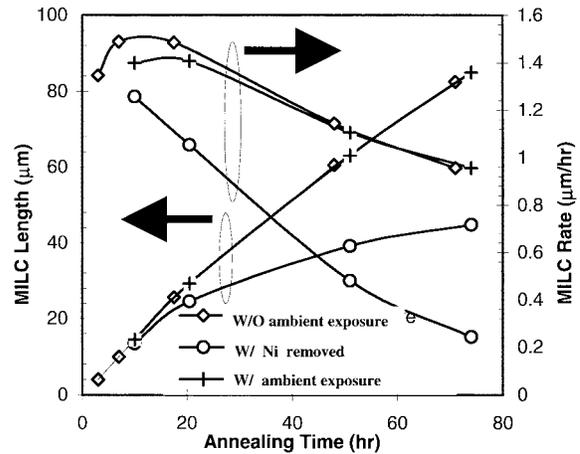


Fig. 5. The dependence of the MILC length and rate on the heat treatment time, with or without the Ni source removed.

significantly slower than those of the samples without the Ni removed.

Since the samples have been taken out of the furnace after the 3-h heat treatment and before receiving the extended heat treatment, it is not clear if the exposure to the ambient affected the MILC. The MILC lengths and rates of the samples without the ambient exposure are also compared in Fig. 5 to those with the exposure. No significant difference was detected.

IV. DISCUSSION

The reasons for the decreasing MILC rate upon extended heat treatment were studied by annealing some α -Si samples for 70 h at 500 °C prior to the Ni deposition. As shown in Fig. 6, the MILC lengths on the samples with the pre-annealing are significantly shorter than those on the samples without, especially upon extended heat treatment. This is true even for the samples covered by LTO during the pre-annealing and the heat treatment. Therefore it is unlikely that the reduction in the MILC rate is caused by the gradual

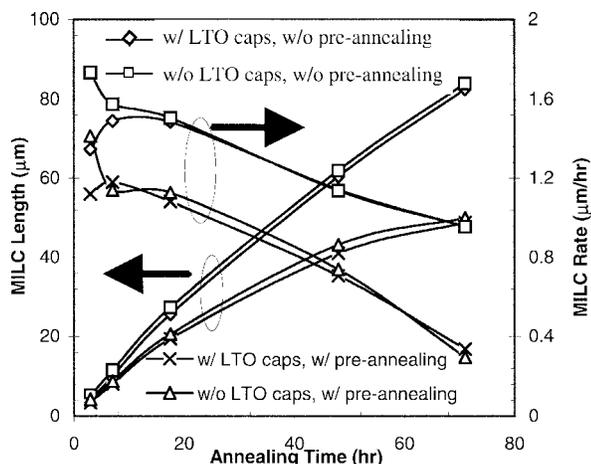


Fig. 6. The dependence of the MILC length and rate on the heat treatment time, with or without the pre-annealing.

introduction of such contaminants as oxygen or metals during the pre-annealing or the extended heat treatment.

Though both Raman spectroscopy and X-ray diffraction results indicated the silicon films remained amorphous even after 140 h of annealing, the effects on the MILC rate indicated that microscopic changes in the α -Si nevertheless has occurred.

One possibility is the change in the hydrogen content in the film. It has been determined using SIMS that the hydrogen content in the LPCVD α -Si film, after being annealed for 100 h at 500 °C, decreased by a factor of about 1.8. Since the presence of hydrogen is known to stabilize α -Si films, as indicated by the higher crystallization temperature of α -Si:H films [2], a lower hydrogen content should result in a less stable film, hence a faster MILC rate at a given temperature.

Alternatively, it has been argued that the activation energy for MIC or MILC is the free energy difference between crystalline Si and α -Si [11]. After the pre-annealing, the atomic rearrangement in the α -Si resulted in a reduction in the energy difference, hence also the MILC rate. Perhaps this is also the reason why in the work of Hong *et al.* [12], a significantly higher temperature is required for the secondary crystallization of polycrystalline silicon than for MIC of α -Si. Therefore, we propose that the continuous microscopic rearrangement of the atoms in the α -Si during the extended heat treatment is largely responsible for the downward drift of the MILC rate.

Interestingly, similar slopes are obtained for the four traces of the MILC rates upon extended heat treatment and, independent of the heat treatment time, the MILC lengths of the samples without the LTO caps are always 1–2 μm longer than those of the samples with the LTO caps. This is why, at the initial stage of the heat treatment, the MILC rates of the samples with the LTO caps diverged from those of the samples without.

Furthermore, it can be seen that the MILC rate ($\sim 1 \mu\text{m/h}$) after 70 h of extended heat treatment of the samples without the pre-annealing is about 20% slower than the initial MILC rate ($\sim 1.2 \mu\text{m/h}$) of the samples with the 70-h pre-annealing. This indicates other secondary mechanisms, in addition to the changing state of the α -Si, are needed to fully account for the decrease of the MILC rate upon extended heat treatment.

It has been shown in Fig. 5 that after the removal of the original Ni coverage, the MILC rate became much smaller and decreased much faster upon extended heat treatment. Since it is highly unlikely that the plasma etching process itself changed the crystallinity of the α -Si film or introduced any significant contaminants, a probable explanation is that the supply of Ni to the crystallization front, possibly via a diffusion mechanism, affected the MILC rate. In the absence of a source of Ni, the finite solubility of Ni in the crystallized Si gradually depletes Ni from the crystallization front and eventually slows down the MILC rate. A divergent diffusive flux could also provide a possible explanation for the dependence of the MILC rate on the radii of curvature of the Ni disc patterns.

V. SUMMARY

Ni induced lateral crystallization of α -Si has been studied by selective deposition of Ni on thin films of α -Si. The MILC rate was observed to slow down upon extended heat treatment and the MILC length was found to increase with the radii of the Ni disc patterns. Our results indicated that the changing state of the α -Si is largely responsible for the reduction in the MILC rate. The dependence on the radii of the Ni discs and the effects of the absence of the Ni source are explained in terms of a diffusive Ni flux in the crystallized Si during the heat treatment.

ACKNOWLEDGMENT

The authors gratefully thank Dr. J. Xie for the Ni deposition and Dr. P. Wong for the SIMS analysis. M. Wong would like to acknowledge Professor S. S. Lau of the University of California at San Diego for suggesting the possibility that the α -Si might be changing during an extended heat treatment.

REFERENCES

- [1] G. Liu and S. J. Fonash, "Selective area crystallization of amorphous silicon films by low temperature rapid thermal annealing," *Appl. Phys. Lett.*, vol. 55, no. 7, pp. 660–662, 1989.
- [2] Y. Kawazu, H. Kudo, S. Onari, and T. Arai, "Low temperature crystallization of hydrogenated amorphous silicon induced by nickel silicide formation," *Jpn. J. Appl. Phys.*, vol. 29, pp. 2698–2704, 1990.
- [3] G. Liu and S. J. Fonash, "Polycrystalline silicon thin film transistor on Corning 7059 glass substrate using short time, low temperature processing," *Appl. Phys. Lett.*, vol. 62, no. 20, pp. 2554–2556, 1993.
- [4] S. Y. Yoon, K. H. Kim, C. O. Kim, J. Y. Oh, and J. Jang, "Low temperature metal induced crystallization of amorphous silicon using a Ni solution," *J. Appl. Phys.*, vol. 82, no. 11, pp. 5865–5867, 1997.
- [5] Z. Jin, G. A. Bhat, M. Yeung, H. S. Kwok, and M. Wong, "Solid-phase reaction of Ni with amorphous SiGe thin films," *Jpn. J. Appl. Phys. Lett.*, vol. 36, no. 12B, pp. L1637–L1640, 1997.
- [6] S. W. Lee, Y. C. Jeon, and S. K. Joo, "Pd induced lateral crystallization of amorphous Si thin films," *Appl. Phys. Lett.*, vol. 66, no. 13, pp. 1671–1673, 1995.
- [7] S. W. Lee and S. K. Joo, "Low temperature poly-Si thin film transistor fabrication by metal-induced lateral crystallization," *IEEE Electron Device Lett.*, vol. 17, pp. 160–162, Apr. 1996.
- [8] G. A. Bhat, Z. Jin, H. S. Kwok, and M. Wong, "Effects of longitudinal grains on the performance of MILC TFT's," *IEEE Electron Device Lett.*, to be published.
- [9] ———, "The effects of MIC/MILC interface on the performance of MILC-TFT's," in *Dig. 56th Annu. Device Research Conf.*, June 22, 1998, pp. 110–111.
- [10] Z. Jin, G. A. Bhat, M. Yeung, H. S. Kwok, and M. Wong, "Ni induced crystallization of amorphous Si thin films on SiO₂," *J. Appl. Phys.*, vol. 84, no. 1, pp. 194–200, 1998.

- [11] C. Hayzelden and J. L. Batstone, "Silicide formation and silicide-mediated crystallization of nickel-implanted amorphous silicon thin films," *J. Appl. Phys.*, vol. 73, no. 12, pp. 8279–8289, 1993.
- [12] Q. Z. Hong, S. Q. Hong, F. M. D'Heurle, and J. M. E. Harper, "Thermal stability of silicide on polycrystalline Si," *Thin Solid Films*, vol. 253, pp. 497–484, 1994.



Zhonghe Jin was born in Zhejiang Province, China, in January 1970. He received the B.S. degree in 1991, the M.S. degree in 1994, and the Ph.D. degree in 1998, all from the Department of Information Science and Electronic Engineering (ISEE), Zhejiang University, China.

He stayed with the ISEE Department after graduation and engaged in the research and development of silicon based micro-machining technologies and sensors. From March 1996 to February 1998, he was a visiting research associate at the Department of

Electrical and Electronic Engineering, Hong Kong University of Science and Technology, Hong Kong, where he engaged in the research of low-temperature polycrystalline thin film transistors and related materials.

Keith Moulding received the B.Sc. and Ph.D. degrees from the University of Essex, U.K., investigating nonlinear optical glasses and optical fibers using transmission electron microscopy.

He is currently coordinating the electron microscopy facility at The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. Research interests have included scanning and transmission electron microscopy of sol-gel thin films, ancient ceramic glasses and micro-structure determination in the scanning electron microscope.

Hoi S. Kwok (S'73–M'78–SM'84) received the Ph.D. degree from Harvard University, Cambridge, MA, in 1978.

He was on the faculty at the State University of New York at Buffalo from 1980 to 1983. He joined the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, as a Professor in 1993.



Man Wong (S'83–M'84) was born in Beijing, China. From 1979 to 1984, he studied at the Massachusetts Institute of Technology, where he received the B.S. and M.S. degrees in electrical engineering. From 1985 to 1988, he was at the Center for Integrated Systems at Stanford University, where he received the Ph.D. degree, also in electrical engineering.

He then joined the Semiconductor Process and Design Center of Texas Instruments, Dallas, TX, and worked on the modeling and development of

the metallization systems for 64M DRAM and the development of dry/vapor cleaning processes. In 1992, he joined the faculty of the Department of Electrical and Electronic Engineering at the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. His current research interests include advanced device fabrication technology, novel device structures and materials, thin film transistors, display technologies, and micro-machines.

Dr. Wong is a member of Tau Beta Pi, Eta Kappa Nu, and Sigma Xi.