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PROCESSES AND PROCESS DEVELOPMENT IN TAIWAN

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ABSTRACT

Silicon material research in ROC parallels its development in electronic industry. This paper gives a brief outline of the historical development in ROC silicon material research. Emphasis is placed on the recent Silane Project managed by the National Science Council, ROC, including project objectives, task forces and recent accomplishments. An introduction is also given to industrialization of the key technologies developed in this project.

INTRODUCTION

For a land of such limited resources, R.O.C. in Taiwan has been ranked as one the highest in population density and in economic developments in the past 20 years or so.

It is an intriguing question as to how this island will develop in the future, especially in the electronics and solar inndustries. It could set an example for other developing countries.

A Silane Project managed by National Science Council, R.O.C. was initiated in 1981 with the objective to develop key technologies in solar cell and semiconductor Si materials. This project emphasizes coordination among institutions and an overall management plan for various phases of the developments.

Taiwan has a fair amount of high quality quartzite deposits; the Mining Institute of Industry Technology Research Institute (ITRI) is responsible for the mining deposit survey. This organization is also responsible for the crude - and solar-Si production by the reduction/leaching techniques.

The Applied Chemistry Division of Chung-shan Institute of Science and Technology has developed the technologies for the production and pyrolysis of the silanes ($SiHCl_3$, SiH_2Cl_2 and SiH_4). Pilot production operation is scheduled and will be carried out by the Institute of Chemical Engineering of ITRI.

The Nuclear Instrumentation Division of INER (Institute of Nuclear Energy Research) is responsible for the Chemical Vapor Deposition (CVD) processes, and for photovoltaic solar cell and module fabrication. A group from the Mechanical Research Laboratories is currently engaged in the development of a LPCVD industrial system for epitaxial Si production.

Polycrystalline Si production by gas assisted solidification has been developed at the Tsing-Hua University, and solar modules made from this material will be installed in the Yu-Shan National Park Electricity Development Project.

Amorphous Si solar cell prepared by glow-discharge has been successfully developed for consumer electronics by the Energy Research Laboratory of ITRI. Pilot production technology is under development.

A strong five-team characterization group has been assembled in Tsing Hua Unviersity to support the analysis of silane and Si materials by chemical, defect, electrical and surface measurements; particular emphasis is given to the correlations among these analyses.

This project has also promoted the joint venture of a 10 MW ribbon Si solar cell production in Taiwan. The goal is to develop the key technologies for silicon materials and to establish the foundation for prospective semiconductor Si materials and solar cell industries by 1990.

HISTORICAL

Table 1 depicts a brief historical outline of semiconductor silicon development in Taiwan.

In view of the increasing world-wide demand for ultra-pure silicon, a project was initiated in 1971 at the Department of Mechanical Engineering, National Taiwan University, by the late Prof. T.H. Loh to investigate high-purity silicon-manufacturing processes [1,2]. This work was terminated after the death of Prof. Loh. The activity in high-purity silicon production was soon resumed by the National Science Council (formerly National Research Council) by granting a joint project to the Chemistry and Physics Departments of National Tsing Hua University (NTHU) for studying the techniques for the chemical purification of silicon [3-5] and for single crystal silicon growth. Unfortunately, these efforts were not continued, either due to the limitations of material characterization capability or to a shift in research funding priority.

At almost the same time, the Electronic Research and Service Organization (ERSO) was established in the Industrial Technology Research Institute (ITRI) with the objective of developing IC technology. The establishment of ERSO in ITRI signified a temporal shift in interest from silicon material research to device-related research and development. An ion implanter was provided to the Physics Department of NTHU in 1976.

Tatung Co. was the first industrial establishment to initiate silicon material research by setting up an electronic R&D division in 1977. In 1978 semiconductor silicon wafers from single crystals prepared by the Floating Zone process were on the market for testing. In 1981 the Sino-American Silicon Product Incorporation was established to produce silicon wafers by the Czochralski Process. Currently, these two companies supply a large portion of Si wafers for the local diode--and transistor--industry; more than 70% of the world-wide production of diodes is in Taiwan. In 1981, an interdisciplinary project for the application of silane was initiated by the National Science Council, ROC, with the aim of developing silicon technology in Taiwan.

It is apparent as outlined in Table 1 that silicon material research in Taiwan blew in two waves. The first one was in the early 1970s and the second around the turn of 1980. The description of our recent advances in silicon material research will focus on the Silane Project.

SILANE PROJECT

A distinct feature of this project is its organization and management. The overall program of the project is shown in Fig. 1.

The first phase of the project (1981-1985) will end this year. To date, this project has accomplished the followng objectives: (1) a complete survey of the quartzite deposits in eastern, central and northern Taiwan; (2) production of metallurgical-grade silicon (MG-Si), upgraded MG-Si (UMG-Si) and solar-grade Si (SoG-Si); (3) production and purification of $SiHCl_3$ as in the Siemens Process and production of $SiHCl_3$, SiH_2Cl_2, and SiH_4 by the Chung-Shan Inst. of Science and Technology (CSIST) process; (4) production of 4" diameter multicrystalline Si (Poly-Si) wafers by Gas-Assisted-Solidification (GAS); (5) development of chemical vapor deposition (CVD) technology for silicon epitaxial layer growth; and (6) establishment of the capabilities for chemical (ppb level), structural, electrical, and surface analyses. The second phase (1985-1988) of this project is aimed at the development of pilot production technologies.

1. Production and Chemical Upgrading of Metallurgical-grade Silicon [6]

A detailed survey of high purity siliceous raw materials in Taiwan indicated that the four major types of silica deposits - vein quartz, quartzite, metamorphosed chert and sandstone - are economically feasible for silicon production [7]. MG-Si has been produced from vein quartz using an in-house designed batch-type single electrode submerged arc furnace. The MG-Si thus produced was shown to have an average grade of better than 98% silicon content.

Direct chemical upgrading of MG-Si was performed using a two-stage acid leaching/magetic separation.

After the two-stage acid leaching, the contents of boron and phosphorus were both below 2 ppmw and the total impurity was below 90 ppmw level, but the C content was still not yet acceptable.

The technique of directional solidification to obtain further purification was investigated, and solar-grade Si has been produced (Table 2).

In addition to melting experiments for MG-Si production, silicon recovery in powder form by reduction of a fluosilicate with an organic reductant has also been tried. Preliminary results from a number of exploratory experiments were encouraging.

2. Silane Production/Pyrolysis

Trichlorosilane has been synthesized by chlorination of MG-Si with anhydrous HCl gas in a 34 mm x 60 cm reactor heated with a tube furnace. Reaction conditions, such as temperature, HCl feed rate, Si particle size and Si packing-weight, have been optimized and a routine GC method for analysis of SiH_xCl_{4-x} ($x = 0-4$) was established. Crude $SiHCl_3$ was then purified with both multifractional distillation and chemical methods. A comparison of trace impurities in a commercially available $SiHCl_3$ and those from the project is shown in Table 3. The analytical results indicate the B and P contents in the purified $SiHCl_3$ are laboratory environment-sensitive.

Moreover, the hydrogenation reaction of $SiCl_4$ and the disproportionation reactions of $SiHCl_3$ and SiH_2Cl_2 at "normal" pressure with special treated resin (not A-21) as catalyst were studied at CSIST. The gas-solid reaction was shown to be the dominant feature. Good product yields have been achieved for both reactions. The SiH_2Cl_2 and $SiHCl_3$ products were used for epitaxial growth in an in-house developed CVD system (vide infra). Diodes and transistors having good performance characteristics were made from these epi-layers with high production yields. A 2" diameter fluidized bed reactor (FBR) was constructed for the pyrolysis of SiH_4, and ~400 to 500 μm grains have been obtained. However, contamination from the reaction wall is still a problem.

3. Growth of Epitaxial Layer by Chemical Vapor Deposition [9]

A versatile horizontal CVD system was designed and constructed for silicon epitaxial layer growth. Silicon epi-layers have been successfully grown from this system by hydrogen reduction of SiH_2Cl_2 and $SiHCl_3$ (prepared by the Silane Group). Material characterization and production yields of planar diodes and small signal transistors made from these epi-wafers (Table 4) show that the epi-wafers are industry-applicable. Gettering processes, such as high dose back surface oxygen ion implantation and a mechanical damage followed by heat treatment, have been experimentally used to obtain further improvements in the crystallographic perfection of the epi-layers. Conditions for epi-layer growth on gettered, front surface denuded substrates have been shown to significantly decrease microdefect density.

4. Poly-Si Production [10]

Poly-Si ingots have been produced by a self-designed GAS system. The GAS process is intended to be a low cost process for producing material for solar cells.

SoG-Si was cast in silicon nitride coated quartz crucibles by forced freezing initiated by means of a cold finger located at the bottom of the crucible. Both the heating temperature and the gas flow to the cold finger are microprocessor-controlled. Poly-Si crystals with large elongated grains have been successfully produced. An etched wafer and a solar cell fabricated from a poly-Si crystal are shown in Fig. 2. Analytical results and electrical properties measured on various areas of a wafer cut from one of the poly-Si ingots grown by this GAS system are shown in Tables 5 and 6.

The detailed kinetics of the grain growth have beesn studied by varying (1) the cooling gas, (2) the heating cycles of the crucibles, (3) the maxium He flow rate, and (4) the He flow/time profile.

5. Fabrication of Amorphous Si Solar Cells [11]

The project is currently endeavoring to develop a glow-discharge CVD process for fabricating amorphous silicon-hydrogen (a-Si:H) solar cells. a-Si:H solar cells with efficiency of 4% for consumer products have been routinely produced.

In-depth studies of the stability of a-Si:H have been carried out. When films are subjected to prolonged illumination, it was found from FT-IR that distinct transitions could occur among various bonds and from EPR that dangling bonds could be produced. A model based on bond-breaking of the three-center bonds was proposed (Fig. 3). [12]

6. Material Characterization

The analytical methods for the determination of trace impurities in both silane and elemental silicon at about ppb levels have been established by two laboratories (NTHU and INER). The methods employed include ICP, DCP, NAA, FAAS and UV/VIS.

Analytical methodology to fulfil the specific requirements of rapidity, sensitivity and depth profile for better characterization of silicon materials is being studied further in the present study. The main accomplishments are: (1) establishment of the ICP-AES technique for achieving fast, reliable and sensitive determinations of over 20 elements in silicon and silane samples by optimally combining various instrumental parameters (optical system, RF power, Ar-gas flow, etc.) with a chemical pretreatment step; (2) development of pretreatment techniques for the concentration of various trace impurities in dichloro- and trichloro-silanes by adding adducting materials (such as Lewis acids or bases) to react with B, P and As in the samples. This is followed by sensitive instrumental determination. B, P, As and some metallic impurities can be effectively determined down to 10^{-9}g/g; (3) development of methods for the determination of impurity and dopant concentrations (B, P and As) in silicon semiconductor as a function of depth. The method established is based on the anodic oxidation of the silicon sample followed by sensitive instrumental determination of the dissolved oxide layer; the results are then compared with those from physical evaluations; and (4) preliminary study of the determination of carbon in silicon materials by a chemical analytical method. The method consists of steps for converting the carbon in the dissolved silicon materials into carbon dioxide followed by the quantitative determination by conductometry.

Defect and electrical characterization for semiconductor silicon has been routinely carried out following the ASTM Standards. A reflection Lang X-ray topography camera has recently been built and a SEM laboratory for surface characterization was set up.

A TEM/cross-section technique was developed. Improvement of a SEM to run in the EBIC mode was done to determine the carrier lifetimes (Fig. 4). A MOS C-V method was also used to determine the carrier lifetimes of poly-Si crystals.

A major project has been carried out using TEM and SEM for the study of microstructures and defects; the emphasis was placed on type, quantity, and characteristics. The electrical characteristics, including resistivities, mobilities and lifetimes, have been determined. A coordinated study, including chemical, structural, electrical, and surface characterization on poly-Si crystals grown by GAS, has been under way. A numerical scheme employing non-parametric statistics was developed to investigate correlations among them. Effects on sample pretreatments, as well as of gettering processes, on changes of defect characteristics have been studied. Results indicated that there are correlations between the oxygen content and the carrier lifetime.

7. Economic Analysis [13]

Cost and benefit analyses have been carried out based on a preliminary process design for production plants of 1,000 ton/year capacity for the conventional polysilicon process and the U.C.C. process. A power law scaling factor and a sizing model were used to estimate the capital investment. The results indicate that the order of importance of specific cost parameters influencing product cost is plant investment, utilities, raw materials and labor for conventional polysilicon process; the order for the

U.C.C. process is utilities, plant investment, raw materials and labor (Fig. 5). The conclusion is that the plant site should be chosen where the cost of utilities and raw materials are the lowest.

8. Application Project

In 1985, an application project using PV modules made from poly-Si and ribbon Si solar cells was formulated to help in the promotion of local PV industry. A total 2.6 MW electricity is needed for the Yu-shan National Park at specified sites. System experience of ERL of ITRI will be directly applicable to this project.

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Table 1. A Brief Historical Outline of Semiconductor Silicon-related R&D in Taiwan, ROC.

Year	Institution or Organization	Interest
1966	Semiconductor Resarch Center, National Chiao Tung Univ.	IC and Semiconductor research
1971	Dept. of Mechanical Engineering National Taiwan Hua Univ.	High-purity Silicon-manufacturing Process development
1973	Chemistry Department National Tsing Hua Univ.	Chemical purification of Silicon Project
1973	Physics Department National Tsing Hua Univ.	Single crystal silicon growth project
1974	Electronic Research and Service Organization, Industrial Technology Research Institute	IC technology development
1976	Physics Department National Tsing Hua Univ.	Ion implantation
1978	Electronic R&D Division Tatung Co.	Semiconductor silicon wafer production (FZ)
1981	Sino-American Silicon Product Incorporation	Semiconductor silicon wafer production (CZ)
1981	National Science Council	Application of Silane Project.
1983	Four companies start-up in Hsin-chu Science Park	VLSI

Table 2 Analytical data of SoG-Si produced by chemical leaching/GAS methods

Sample / Element	Metallurgical Grade Si	Ultimate Metallurgical Grade Si			Solar Grade Si	
		1st Leaching	2nd Leaching	Analytical Method	Grown by G.A.S.	Analytical Method
Al	6300ppm	250ppm	130ppm	NAA, ICP	< 6ppb	NAA
Fe	2800ppm	32ppm	2.5ppm	ICP	< 4ppb	NAA
Ca	2100ppm	13ppm	7.4ppm	ICP	<98ppb	NAA
Cr	140ppm	1.6ppm		ICP	< 6ppb	NAA
Co	77ppm			ICP	< 1ppb	NAA
Mn	0.5ppm	0.5ppm		ICP	< 1ppb	NAA
Cu	37ppm			ICP	< 1ppb	NAA
B	25ppm	19ppm	19ppm	ICP	<81ppb	ICP
P	23ppm	16ppm	16ppm	UV/VIS	<36ppb	UV/VIS
As	18ppm	10ppm		Polarography	<14ppb	NAA

*1. Starting material MG-Si from Elkem a/s, Norway
2. 1st stage leaching: $HF (12\%) + HCl (9\%)$, $80^{\circ}C$, ambient condition, 1hr.
   2nd stage leaching: $HF (12\%) + HCl (9\%) + C_2H_2O_4 (10\%)$, $150^{\circ}C$, under pressure, 1hr.
3. Crystal Growth: GAS (Gas Assisted Solidification)
4. Product: Solar-Grade Silicon, Polycrystalline Si ingot.

Table 3. A comparison of trace impurities (in ppb) in trichlorosilane (TCS) Prepared by Silane Group and that from commercial source.

Sample*	P	Al	Mn	Fe	Zn	Ag	Cu	Mg
Commerical	<1.2	156	<2	59	27	<1	<37	35
TCS-1	20	10	<20	31	<16	<10	<12	33
TCS-2	15	194	<9	44	<9	<4	<4	30

* TCS-1 and TCS-2 represent trichlorosilane from two different runs.

Table 4. A comparison of characteristics and product yields (%) of small signal transistors (2N3906) fabricated from commercial epi-wafer and epi layer grown from commercial TCS and TCS-2 from Silane Group*.

Characteristics	A	B	C
BV_{EBO}>5.5 V (at I_{EBO} = 10 A)	94%	84%	83%
BV_{CBO}>44 V (at I_{CBO} = 10 μA)	75	56	35
I_{CBO}>10 nA (at V_{CB} = 30 V)	76	52	49
BV_{CEO}>44 V (at I_{CEO} = 1 mA)	80	65	34
HFE>80 (at V_{CE} = 1 V, I_C = 10 mA)	96	92	88

* A, from commercial epi-wafer; B, epi layer prepared from commercial TCS; C, epi layer prepared from TCS-2 (Table 3).

Table 5. Analytical Results of a poly-Si wafer prepared from ingot grown by GAS method*.

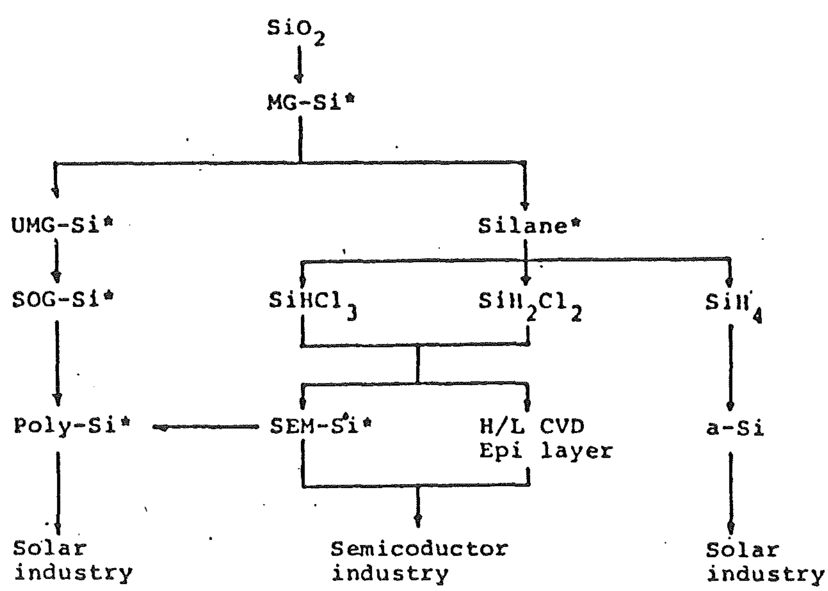
Element	S	33	$3\bar{3}$	$\bar{1}3$	$\bar{1}\bar{3}$	32	$3\bar{4}$	$\bar{1}2$	$\bar{1}\bar{4}$
B (ppb)	0.5	-	-	-	-	<2	<2	<2	<2
P	0.4	-	-	-	-	<14	<14	<14	<14
Ca	3.7	350	160	200	60	71	567	97	157
Mg	0.5	210	30	70	14	6	82	10	7
Fe(ppm)	0.9	0.3	0.9	1.0	1.0	7	7	14	7
Al	1.9	-	-	-	-	<21	<21	35	<21

* S represents source material and numbericals designate areas of the wafer. Results of 33 - $\bar{1}\bar{3}$ from NTHU group and those of 32 - $\bar{1}\bar{4}$ from INER. -, no results due to sample loss.

Table 6. Electrical characterization of a poly-Si wafer prepared from ingot grown by GAS method*

Properties	23	$2\bar{3}$	$\bar{2}3$	$\bar{2}\bar{3}$
Thickness (μm)	687	686	684	678
Hall mobility (cm^2/V·sec)	96.6	79.8	142	100
Hall resistivity (Ω-cm)	2.42	3.08	1.34	2.03
Carrier conc. ($10^{16}/cm^3$)	2.7	2.5	3.2	3.0
Diffusion length (μm)	6	2	4	6
Carrier lifetime (μs)	0.33	0.45	0.4	0.48
Carbon (10^{17} atom/cm^3)	1.51	0.91	1.62	0.67
Oxygen (10^{17} atom/cm^3)	2.15	0.80	0.56	-

* Samples given in numerical represent area code on the wafer.



* Subject to material characterization such as
chemical analysis
structure characterization
electrical characterization
surface characterization
economic analysis

Fig. 1. Over-all Program of Application of Silane Project.

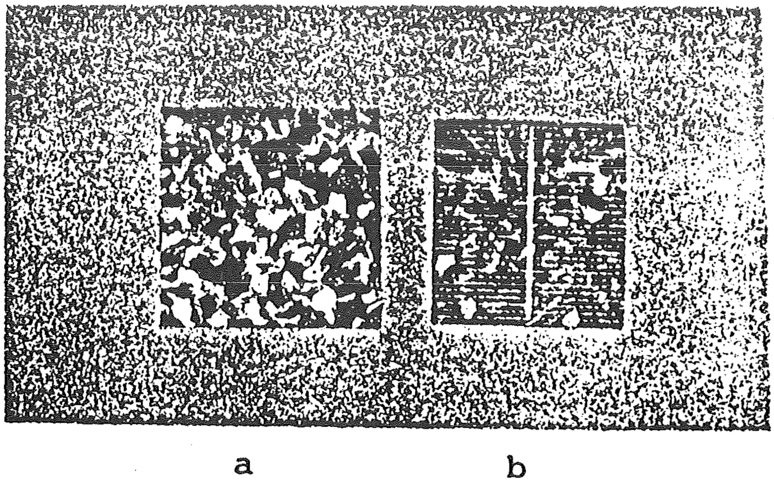


Fig.2. Photographs of a polished GAS Poly-Si wafer (a) and a solar cell fabricated from the wafer (b).

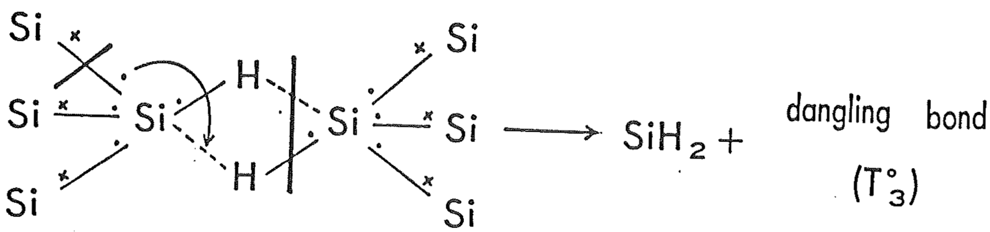
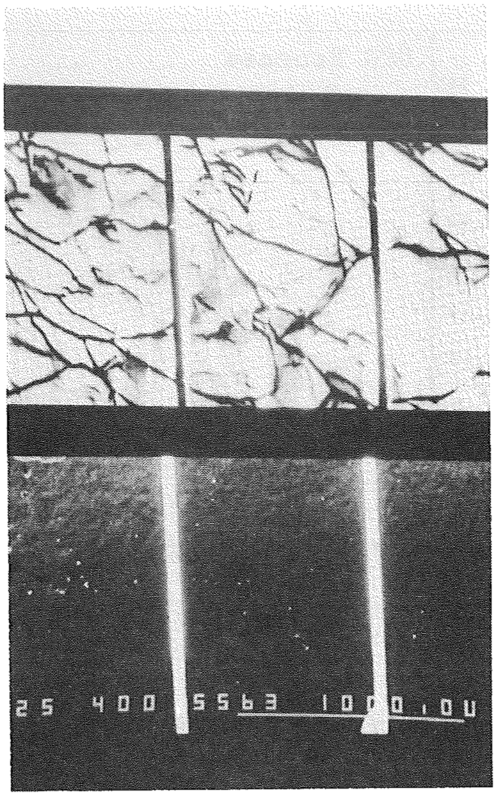


Fig 3. A proposed model to interpret bond change in a-Si:H film



(a)

(b)

Fig. 4(a) EBIC
(b) SEM photograph of a GAS grown Poly:Si solar cell

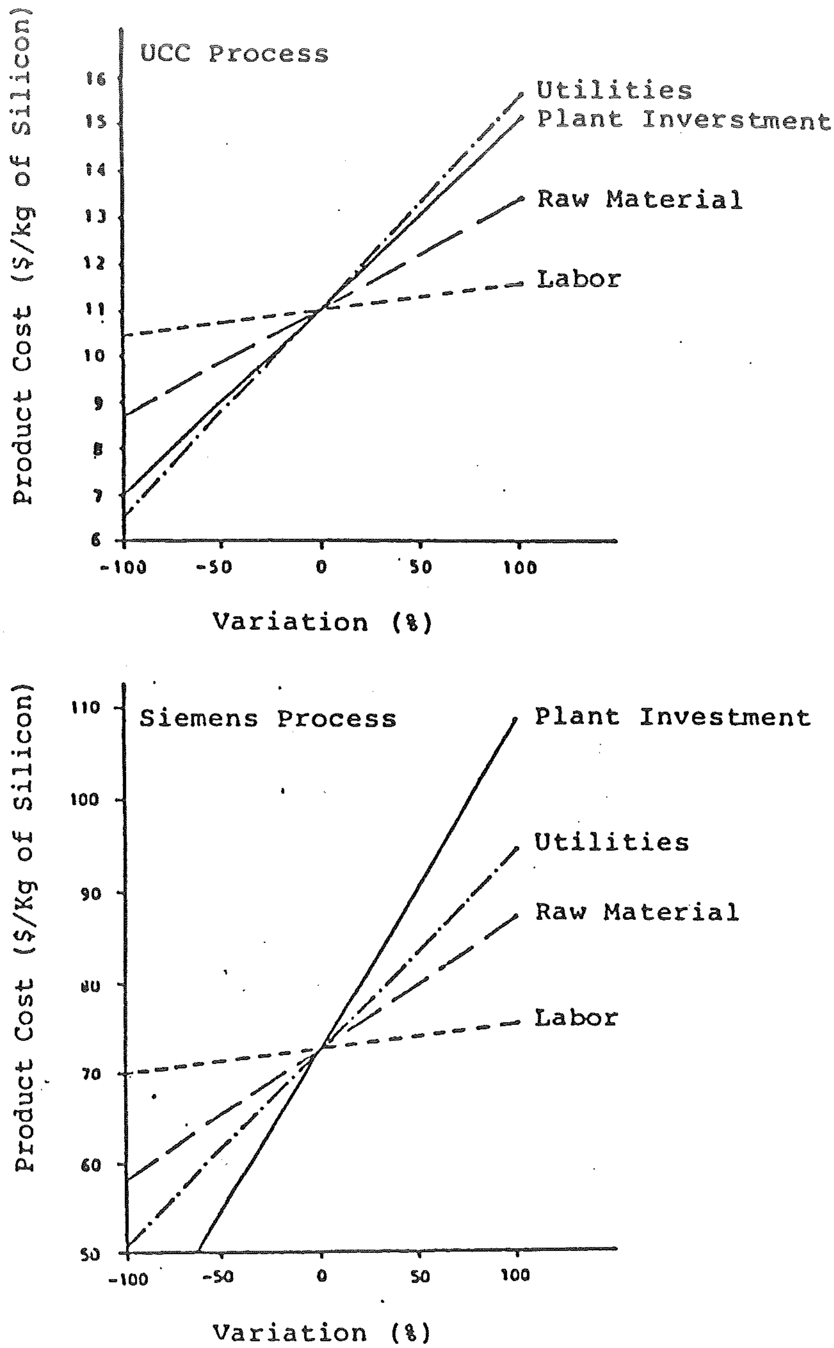


Fig. 5. Cost sensitivity: product cost vs variation.

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DISCUSSION

MAYCOCK: I know that there has been a preliminary announcement that Westinghouse is a venture partner in ribbon production. Do you have a venture partner in amorphous silicon yet?

HWANG: We are developing our own technology and we would also like to use our own technology. Because we are not now in the same technical position as the United States, Japan, or West Germany, we welcome joint ventures also.

MAYCOCK: Who made the amorphous-silicon cell? Was it a laboratory product?

HWANG: It was from the laboratory.

AULICH: Would you comment on the fact that your cost projection on the silicon produced by the modified Union Carbide process is only about $11/kg while the Union Carbide calculations show about $25/kg?

HWANG: I mentioned that the calculation would not be accurate because the data we obtained do not cover the parameters necessary for an accurate calculation. Also, I believe that the cost advantage of production in Taiwan must be taken into account.