

## Contents

**Preface** *xiii*

**Abbreviations** *xv*

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Thin Film Technologies	1
1.2	Birth of Cat-CVD	3
1.3	Research History of Cat-CVD and Related Technologies	4
1.4	Structure of This Book	7
	References	8
<b>2</b>	<b>Fundamentals for Studying the Physics of Cat-CVD and Difference from PECVD</b>	<b>11</b>
2.1	Fundamental Physics of the Deposition Chamber	11
2.1.1	Density of Molecules and Their Thermal Velocity	11
2.1.2	Mean Free Path	13
2.1.2.1	Equation Expressing the Mean Free Path	13
2.1.2.2	Estimation of Diameter of Molecules or Species	14
2.1.2.3	Examples of Mean Free Path	15
2.1.2.4	Interval Time Between the First Collision and the Second Collision	16
2.1.3	Collisions with a Solid Surface	17
2.1.3.1	Collisions with a Solid Surface	17
2.1.3.2	Comparison of Collisions of Molecules in Space with Collisions at Chamber Wall	18
2.1.4	Residence Time of Species in Chamber	19
2.2	Difference Between Cat-CVD and PECVD Apparatuses	20
2.3	Fundamental Features of PECVD	21
2.3.1	Birth of PECVD	21
2.3.2	Generation of Plasma	22
2.3.3	DC Plasma to RF Plasma	23
2.3.4	Sheath Voltage	24
2.3.5	Density of Decomposed Species in PECVD	25
2.3.5.1	Number of Collisions Between Electrons and Gas Molecules	25
2.3.5.2	Number of Decomposed Species in PECVD	26

2.4	Drawbacks of PECVD and Technologies Overcoming Them	28
2.4.1	Plasma Damage	28
2.4.2	Increase of Frequency in PECVD	30
2.4.3	Power Transferring System	31
2.4.4	Large Area Uniformity for Film Deposition	31
2.5	Features of Cat-CVD as Technology Overcoming Drawbacks of PECVD	33
2.A	Rough Calculation of Ranges $\langle R \rangle$ of Si and H Atoms and Defect Range $\langle R_{\text{defect}} \rangle$ Created by Si and H Atoms Implanted with Very Low Energy	35
	References	38
<b>3</b>	<b>Fundamentals for Analytical Methods for Revealing Chemical Reactions in Cat-CVD</b>	<b>41</b>
3.1	Importance of Radical Species in CVD Processes	41
3.2	Radical Detection Techniques	42
3.3	One-Photon Laser-Induced Fluorescence	43
3.3.1	General Formulation	43
3.3.2	Validity of the Assumption of a Two-State System	45
3.3.3	Anisotropy of the Fluorescence	47
3.3.4	Correction for Nonradiative Decay Processes	47
3.3.5	Spectral Broadening	48
3.3.6	Typical Apparatus for One-Photon LIF and the Experimental Results	49
3.3.7	Determination of Rotational and Vibrational State Distributions of Molecular Radicals	52
3.3.8	Estimation of Absolute Densities in One-Photon LIF	53
3.4	Two-Photon Laser-Induced Fluorescence	55
3.5	Single-Path Vacuum Ultraviolet (VUV) Laser Absorption	56
3.6	Other Laser Spectroscopic Techniques	58
3.6.1	Resonance-Enhanced Multiphoton Ionization	59
3.6.2	Cavity Ringdown Spectroscopy	60
3.6.3	Tunable Diode Laser Absorption Spectroscopy	63
3.7	Mass Spectrometric Techniques	63
3.7.1	Photoionization Mass Spectrometry	64
3.7.2	Threshold Ionization Mass Spectrometry	64
3.7.3	Ion Attachment Mass Spectrometry	66
3.8	Determination of Gas-Phase Composition of Stable Molecules	66
3.A	Term Symbols Used in Atomic and Molecular Spectroscopy	67
	References	69
<b>4</b>	<b>Physics and Chemistry of Cat-CVD</b>	<b>77</b>
4.1	Kinetics of Molecules in Cat-CVD Chamber	77
4.1.1	Molecules in Cat-CVD Chamber	77
4.1.2	Comparison with PECVD for Decomposition	80
4.1.3	Influence of Surface Area of Catalyst	81
4.2	What Happens on Catalyst Surfaces – Catalytic Reactions	82

4.3	Poisoning of Surface Decomposition Processes	83
4.4	Gas Temperature Distribution in Cat-CVD Chambers	85
4.5	Decomposition Mechanisms on Metal Wire Surfaces and Gas-Phase Kinetics	86
4.5.1	Catalytic Decomposition of Diatomic Molecules: $H_2$ , $N_2$ , and $O_2$	86
4.5.2	Catalytic Decomposition of $H_2O$	89
4.5.3	Catalytic Decomposition of $SiH_4$ and $SiH_4/H_2$ and the Succeeding Gas-Phase Reactions	89
4.5.4	Catalytic Decomposition of $NH_3$ and the Succeeding Gas-Phase Reactions	90
4.5.5	Catalytic Decomposition of $CH_4$ and $CH_4/H_2$ and the Succeeding Gas-Phase Reactions	91
4.5.6	Catalytic Decomposition of $PH_3$ and $PH_3/H_2$ and the Succeeding Gas-Phase Reactions	92
4.5.7	Catalytic Decomposition of $B_2H_6$ and $B_2H_6/H_2$ and the Succeeding Gas-Phase Reactions	93
4.5.8	Catalytic Decomposition of $H_3NBH_3$ and Release of B Atoms from Boronized Wires	94
4.5.9	Catalytic Decomposition of Methyl-Substituted Silanes and Hexamethyldisilazane (HMDS)	94
4.5.10	Summary of Catalytic Decomposition of Various Molecules on Metal Wires	96
4.6	Si Film Formation Mechanisms in Cat-CVD	96
	References	99
<b>5</b>	<b>Properties of Inorganic Films Prepared by Cat-CVD</b>	<b>105</b>
5.1	Properties of Amorphous Silicon (a-Si) Prepared by Cat-CVD	105
5.1.1	Fundamentals of Amorphous Silicon (a-Si)	105
5.1.1.1	Birth of Device Quality Amorphous Silicon (a-Si)	105
5.1.1.2	Band Structure of Amorphous Materials	106
5.1.1.3	General Properties of a-Si	109
5.1.2	Fundamentals of Preparation of a-Si by Cat-CVD	115
5.1.2.1	Deposition Parameters	115
5.1.2.2	Structural Studies on Cat-CVD a-Si: Infrared Absorption	115
5.1.3	General Properties of Cat-CVD a-Si	117
5.1.4	Deposition Mechanism of a-Si in Cat-CVD Process – Growth Model	125
5.2	Crystallization of Silicon Films and Microcrystalline Silicon ( $\mu c$ -Si)	132
5.2.1	Growth of Crystalline Si Film	132
5.2.2	Structure of Cat-CVD Poly-Si	134
5.2.3	Properties of Cat-CVD Poly-Si Films	138
5.2.4	Si Crystal Growth on Crystalline Si	141
5.3	Properties of Silicon Nitride ( $SiN_x$ )	143
5.3.1	Usefulness of Silicon Nitride ( $SiN_x$ ) Films	143
5.3.2	Fundamentals for the Preparation of $SiN_x$	144

5.3.3	SiN <sub>x</sub> Preparation from NH <sub>3</sub> and SiH <sub>4</sub> Mixture	144
5.3.4	SiN <sub>x</sub> Preparation from Mixture of NH <sub>3</sub> , SiH <sub>4</sub> , and a Large Amount of H <sub>2</sub>	150
5.3.5	Conformal Step Coverage of SiN <sub>x</sub> Prepared from the Mixture of NH <sub>3</sub> , SiH <sub>4</sub> , and a Large Amount of H <sub>2</sub>	153
5.3.6	Cat-CVD SiN <sub>x</sub> Prepared from HMDS	155
5.4	Properties of Silicon Oxynitride (SiO <sub>x</sub> N <sub>y</sub> )	157
5.4.1	SiO <sub>x</sub> N <sub>y</sub> Films Prepared by SiH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> , and O <sub>2</sub> Mixtures	157
5.4.2	SiO <sub>x</sub> N <sub>y</sub> Films Prepared by HMDS, NH <sub>3</sub> , H <sub>2</sub> , and O <sub>2</sub> Mixtures	161
5.5	Properties of Silicon Oxide (SiO <sub>2</sub> ) Films Prepared by Cat-CVD	164
5.6	Preparation of Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> ) Films by Cat-CVD	166
5.7	Preparation of Aluminum Nitride (AlN) by Cat-CVD	168
5.8	Summary of Cat-CVD Inorganic Films	170
	References	171
<b>6</b>	<b>Organic Polymer Synthesis by Cat-CVD-Related Technology – Initiated CVD (iCVD)</b>	<b>179</b>
6.1	Introduction	179
6.2	PTFE Synthesis by Cat-CVD-Related Technology	181
6.2.1	Select Characteristics and Applications of CVD PTFE Films	182
6.2.2	Influence of the Catalyzing Materials for PTFE Deposition	186
6.3	Mechanistic Principles of iCVD	187
6.3.1	Initiators and Inhibitors	188
6.3.2	Monomer Adsorption	189
6.3.3	Deposition Rate and Molecular Weight	191
6.3.4	Copolymerization	191
6.3.5	Conformality	193
6.4	Functional, Surface-Reactive, and Responsive Organic Films Prepared by iCVD	194
6.4.1	Polyglycidyl Methacrylate (PGMA): Properties and Applications	203
6.4.2	iCVD Films with Perfluoroalkyl Functional Groups: Properties and Applications	205
6.4.3	Polyhydroxyethylacrylate (PHEMA) and Its Copolymers: Properties and Applications	208
6.4.4	Organosilicon and Organosilazanes: Properties and Applications	212
6.4.5	iCVD of Styrene, 4-Aminostyrene, and Divinylbenzene: Properties and Applications	217
6.4.6	iCVD of EGDA and EGDMA: Properties and Applications	219
6.4.7	Zwitterionic and Polyionic iCVD Films: Properties and Applications	221
6.4.8	iCVD “Smart Surfaces”: Properties and Applications	222
6.5	Interfacial Engineering with iCVD: Adhesion and Grafting	227
6.6	Reactors for Synthesizing Organic Films by iCVD	230
6.7	Summary and Future Prospects for iCVD	232
	References	235

<b>7</b>	<b>Physics and Technologies for Operating Cat-CVD Apparatus</b>	<b>249</b>
7.1	Influence of Gas Flow in Cat-CVD Apparatus	249
7.1.1	Experiment Using a Long Cylindrical Chamber for Establishing Quasi-laminar Flow	249
7.1.2	Dissociation Probability of $\text{SiH}_4$ Derived from a Cylindrical Chamber	251
7.2	Factors Deciding Film Uniformity	253
7.2.1	Equation Expressing the Geometrical Relation Between Catalyzer and Substrates	253
7.2.2	Example of Estimation of Uniformity of Film Thickness	254
7.3	Limit of Packing Density of Catalyzing Wires	255
7.4	Thermal Radiation from a Heated Catalyzer	256
7.4.1	Fundamentals of Thermal Radiation	256
7.4.2	Control of Substrate Temperatures in Thermal Radiation	257
7.4.3	Thermal Radiation in CVD Systems	260
7.5	Contamination from a Heated Catalyzer	261
7.5.1	Contamination of Catalyzing Materials	261
7.5.2	Contamination from Other Impurities	262
7.5.3	Flux Density of Impurities Emitted from Heated Catalyzers	265
7.6	Lifetime of Catalyzing Wires and Techniques to Expand Their Lifetimes	266
7.6.1	Introduction	266
7.6.2	Silicide Formation of W Catalyzer	266
7.6.3	Silicide Formation of Ta Catalyzer	273
7.6.4	Suppression of Silicide Formation by Carburization of W Surface	274
7.6.5	Ta Catalyzer and Method for Extension of Its Lifetime	275
7.6.6	Lifetime Extension by Using TaC	276
7.6.7	Lifetime Extension by Using Other Ta Alloys	277
7.6.8	Lifetimes of W Catalyzer in Carbon-Containing Gases	278
7.6.9	Long-Life Catalyzer Used in <i>i</i> CVD	280
7.7	Chamber Cleaning	281
7.8	Status of Mass Production Machine	283
7.8.1	Cat-CVD Mass Production Machine for Applications in Compound Semiconductors	283
7.8.2	Cat-CVD Mass Production Apparatus for Large Area Deposition	284
7.8.3	Cat-CVD Apparatus for Coating of PET Bottles	287
7.8.4	Prototypes for Any Other Mass Production Machine	288
	References	289
<b>8</b>	<b>Application of Cat-CVD Technologies</b>	<b>293</b>
8.1	Introduction: Summarized History of Cat-CVD Research and Application	293
8.2	Application to Solar Cells	295
8.2.1	Silicon and Silicon Alloy Thin Film Solar Cells	295

8.2.1.1	Introduction	295
8.2.1.2	Amorphous Silicon Solar Cells	296
8.2.1.3	Amorphous Silicon–Germanium Alloy Solar Cells	297
8.2.1.4	Microcrystalline Silicon Solar Cells and Tandem Cells	302
8.2.1.5	Nanostructured Solar Cells	304
8.2.2	Application to Crystalline Silicon (c-Si) Solar Cells	306
8.2.2.1	Introduction	306
8.2.2.2	Cat-CVD Silicon–Nitride ( $\text{SiN}_x$ )/Amorphous–Silicon (a-Si)-Stacked Passivation	307
8.2.2.3	Cat-CVD $\text{SiN}_x$ /a-Si-Stacked Passivation on Textured c-Si Substrates	310
8.2.3	a-Si and c-Si Heterojunction Solar Cells	312
8.2.3.1	Introduction	312
8.2.3.2	Surface Passivation on c-Si Solar Cells	312
8.3	Application to Thin Film Transistors (TFT)	314
8.3.1	Amorphous Silicon (a-Si) TFT	314
8.3.1.1	General Features of a-Si TFT	314
8.3.1.2	Cat-CVD a-Si TFT: Differences from PECVD a-Si TFT	316
8.3.2	Poly-Si TFT	319
8.4	Surface Passivation on Compound Semiconductor Devices	320
8.4.1	Passivation for Gallium–Arsenide (GaAs) High Electron Mobility Transistor (HEMT)	320
8.4.2	Passivation for Ultrahigh-Frequency Transistors	322
8.4.3	Passivation for Semiconductor Lasers	322
8.5	Application for ULSI Industry	323
8.6	Gas Barrier Films for Various Devices Such as Organic Devices	325
8.6.1	Inorganic Gas Barrier Films, $\text{SiN}_x/\text{SiO}_x\text{N}_y$ , for OLED	325
8.6.2	Inorganic/Organic Stacked Gas Barrier Films	328
8.6.3	Gas Barrier Films for Food Packages	332
8.7	Other Application and Summary of Present Cat-CVD Application	335
	References	336

## 9 Radicals Generated in Cat-CVD Apparatus and Their Application 343

9.1	Generation of High-Density Hydrogen (H) Atoms	343
9.1.1	Generation of High-Density H Atoms	343
9.1.2	Transportation of H Atoms	346
9.2	Cleaning and Etching by H Atoms Generated in Cat-CVD Apparatus	348
9.2.1	Etching of Crystalline Silicon	348
9.2.2	Cleaning of Carbon-Contaminated Surface	350
9.3	Photoresist Removal by Hydrogen Atoms	351
9.4	Reduction of Metal Oxide by H atoms	356
9.4.1	Reduction of Various Metal Oxides	356
9.4.2	Characteristic Control of Metal Oxide Semiconductors by H Atoms	357

9.5	Low-Temperature Formation of Low-Resistivity Metal Lines from Liquid Ink by H Atoms	358
9.6	Low-Temperature Surface Oxidation – “Cat-Oxidation”	360
9.7	Low-Temperature Surface Nitridation – “Cat-Nitridation” of Si and GaAs	365
9.8	“Cat-Chemical Sputtering”: A New Thin Film Deposition Method Utilizing Radicals	372
	References	374
<b>10</b>	<b>Cat-doping: A Novel Low-Temperature Impurity Doping Technology</b>	<b>377</b>
10.1	Introduction	377
10.2	Discovery or Invention of Cat-doping	378
10.3	Low-Temperature and Shallow Phosphorus (P) Doping into c-Si	380
10.3.1	Measurement of Electrical Properties of a Shallow-Doped Layer	380
10.3.2	Measurement of Concentration Profiles of Cat-Doped Impurities by SIMS	383
10.3.3	Estimation of Diffusion Constant	388
10.3.4	Properties of Cat-Doped P Atoms	389
10.3.5	Mechanism of Cat-doping	392
10.3.5.1	Possibility of Diffusion Enhancement by H Atoms	392
10.3.5.2	Vacancy Transportation Model	394
10.3.5.3	Si-Modified Surface Layer Model	397
10.4	Low-Temperature Boron (B) Doping into c-Si	398
10.5	Cat-Doping into a-Si	401
10.6	Feasibility of Cat-Doping for Various Applications	403
10.6.1	Surface Potential Control by Cat-doping Realizing High-Quality Passivation	403
10.6.2	Cat-doping into a-Si and Its Application to Heterojunction Solar Cells	405
	References	407
	<b>Index</b>	<b>411</b>