FORMATION OF SILICON NANOWIRES BY CHEMICAL VAPOUR DEPOSITION TECHNIQUE USING INDIUM CATALYST

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ABSTRACT

Formations of silicon nanowires using aurum and indium catalyst by plasma-enhanced chemical vapour deposition and hot-wire chemical vapour deposition techniques were studied in this work. The depositions were carried out by using a home-built dual-mode plasma-assisted hot-wire chemical vapour deposition system. A tungsten filament with purity of 99.95% was employed for evaporation of aurum or indium wire to form catalyst on a substrate. Silane gas, which was diluted in hydrogen carrier gas was used as a precursor for the growth of the silicon nanowires. Plasma was generated through a power electrode by a radio frequency generator (13.56 MHz), and hot-wire process was initiated by heating the same tungsten filament used for evaporation.

Indium catalyst showed better catalytic effect compared to aurum catalyst for low temperature growth of silicon nanowires. Under the same deposition conditions, aurum catalyst was only able to induce short worm-like nanowires with length ~0.9 μm. Indium catalyst, however, induced higher density of worm-like nanowires with length up to 10 μm. The results showed that the alignment of the nanowires is very dependent on the catalyst size. Large catalyst size tends to induce randomly-oriented worm-like nanowires, while aligned nanowires can be formed by reducing the catalyst size to ≤ 137 nm.

Plasma discharging silane gas created high energetic precursors for the growth of nanowires. As a result, higher radio frequency power produced higher density of nanowires (provided the critical power for nanowire growth is not exceeded). However, crystallinity of the nanowires showed an adverse effect with the radio frequency power, as the energetic ions bombardment can destroy the crystalline structures of the nanowires. Hot-wire chemical vapour deposition is promising for the production of high crystallinity of nanowires due to its ion-free process. The crystallinity of the nanowires was increased with increase in filament temperature. A threshold filament temperature for the growth of silicon nanowires was observed between 1400 and 1500^{o}C. The whisker-like silicon nanowires started to form at filament temperature 1500^{o}C. Further increase in filament temperature can increase the aspect ratio and decrease the kinked structure of the nanowires.

High silane decomposition rate of hot-wire chemical vapour deposition could produce large quantities of silyl radicals for the catalytic growth of nanowires. The uncatalyzed silyl radicals tend to absorb onto the walls of the nanowires and result in the radial growth process. Radial growth of slanting columnar silicon nanocrystallite structures were observed on the nanowires. This contributed to the tapering of the nanowires. The axial and radial growth mechanisms of the indium catalyzed silicon nanowires were studied by varying the deposition time. The axial and radial growth rates of ~280 ± 60 and ~12.0 ± 0.1 nm/min were obtained. The axial and radial growth processes resulted in the formation of crystalline silicon/slanting silicon nanocolumns core-shell nanowires with aspect ratio of ~18 ± 2.

ABSTRAK

Pembentukan silikon nanodawai menggunakan aurum dan indium sebagai mangkin menggunakan kaedah pemendapan wap kimia secara peningkatan plasma dan kaedah pemendapan wap kimia secara pemanasan filamen telah dipelajari. Pemendapan ini dijalankan dengan menggunakan sistem mod dual pemendapan wap kimia secara pemanasan filamen dengan bantuan plasma buatan sendiri. Filamen tungsten berketulenan 99.95% telah digunakan bagi pengewapan dawai aurum dan indium untuk menghasilkan mangkin di atas substrat. Gas silane yang dicairkan dalam gas hidrogen telah digunakan sebagai prekursor untuk pertumbuhan silikon nanodawai. Plasma dijanakan melalui kuasa elektrod oleh penjana frekuensi radio (13.56 MHz) manakala proses pemanasan filamen dimulakan dengan memanaskan filamen tungsten tersebut.

Indium mangkin menunjukkan kesan mangkin yang lebih baik berbanding aurum untuk pertumbuhan silikon nanodawai pada suhu rendah. Aurum mangkin hanya mampu membentuk nanodawai menyerupai cacing pendek (~0.9 μm). Manakala, Indium mangkin mampu membentuk nanodawai yang berketumpatan lebih tinggi dengan panjang saiz sehingga 10 μm. Hasil penyelidikan menunjukkan penjajaran nanodawai amat bergantung kepada saiz mangkin. Saiz mangkin yang besar cenderung membentuk nanodawai menyerupai cacing berorientasi secara rawak, manakala nanodawai menjajar dapat dihasilkan dengan mengurangkan saiz mangkin kepada ≤ 137 nm.

Gas silane yang dinyahcaskan oleh plasma menghasilkan prekursor bertenaga tinggi untuk pertumbuhan nanodawai. Kuasa radio frekuensi yang lebih tinggi menghasilkan ketumpatan nanodawai yang lebih tinggi, jika tidak melebihi had kuasa genting untuk pertumbuhan nanodawai. Walaubagaimanapun, kehabluran nanodawai menunjukkan kesan yang berbeza dengan peningkatan kuasa frekuensi radio kerana hentaman ion bertenaga dapat menghapuskan struktur kristal nanodawai. Pemendapan wap kimia secara pemanasan filamen berpotensi untuk menghasilkan nanodawai kehabluran tinggi disebabkan oleh ion bebas. Kehabluran nanodawai meningkat dengan peningkatan suhu filamen. Nilai ambang suhu filamen bagi pertumbuhan silikon nanodawai telah diperolehi di antara 1400 dan 1500^{o}C. Silikon nanodawai menyerupai misai mula terbentuk pada suhu filamen 1500^{o}C. Lanjutan peningkatan suhu filament dapat meningkatkan nisbah aspek dan mengurangkan kepintalan struktur pada nanodawai.

Kadar penguraian gas silane yang tinggi oleh filamen panas dapat menghasilkan radikal silyl yang berkuantiti besar untuk memangkinkan pertumbuhan nanodawai. Radikal silyl yang tidak termangkin cenderung meresap ke seluruhan dinding nanodawai dan menghasilkan proses pertumbuhan jejarian. Pertumbuhan jejarian bagi struktur silikon nanokristalit yang sendeng telah diperhatikan pada nanodawai. Ini menyumbang kepada penirusan nanodawai. Mekanisma pertumbuhan paksi dan jejarian bagi indium pemangkin silikon nanodawai telah dipelajari dengan mengubah masa pemendapan. Kadar nilai pertumbuhan paksi dan jejarian yang diperolehi adalah ~280 ± 60 dan ~12.0 ± 0.1 nm/min. Proses pertumbuhan paksi dan jejarian menghasilkan pembentukan teras petala nanokolum sendeng silikon nanodawai dengan nisbah aspek sebanyak ~18 ± 2.

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LIST OF SYMBOLS

E_A^{Si}	activation energy of silane
ω	wavenumber/Raman shift
$\Delta\omega$	shifting of crystalline peak from single crystal Si peak
Δz	axial resolution of Raman spectroscopy
d_c	critical size
D_R	crystallite size (Raman)
D_x	crystallite size (X-ray diffraction)
E_ion	ion energy
$\mathrm{I_C/I_{GB}}$	ratio of integrated intensity of crystalline to grain boundary components
k_B	Boltzmann's constant
L	lateral resolution of Raman spectroscopy
l_{Au}	length of aurum wire
l_{In}	length of indium wire
l_{NW}	length of the silicon nanowires
P	deposition pressure
R_{axial}	axial growth rate of silicon nanowires
r_base	base radius of silicon nanowires
$r_\mathrm{c\text{-}nw}$	catalyst size to nanowires diameter ratio
r_{NW}	radius of silicon nanowires
r_o	initial radius/crystalline core radius of silicon nanowires
R_{radial}	radial growth rate of silicon nanowires
r_top	top radius of silicon nanowires
t_d	deposition time
T_f	filament temperature
t_{nuc}	nucleation time
T_p	tapering parameter
T_s	substrate temperature
t_t	plasma treatment time
V	sheath voltage
X_C	crystalline volume fraction
Δr_NW	difference in radius of silicon nanowire
β	silicon nanocolumns tilt angle with respect to direction of incident flux
θ	angle of the X-ray diffraction peak
α	oblique angle of silicon nanowires with the incident flux
θ_{NW}	inclination angle of the silicon nanowires
ρ_{In}	number density of the indium droplets per unit area
ρ_{Si}	number density of silicon nanowires per unit area
ω_o	single crystalline silicon peak position (= 521 $\mathrm{cm^{-1}}$)

LIST OF ABBREVIATIONS

AES	auger electron spectroscopy
at%	atomic percentage
CCD	charge-coupled-detector
c-Si	crystalline silicon
CVD	chemical vapour deposition
DI	Deionized
ECR	electron-cyclotron resonance
EDX	energy-dispersion X-ray spectroscopy
FESEM	field emission scanning electron microscopy
FET	field effect transistor
FTIR	Fourier transform infrared
FWHM	full width at half maximum
$HF/Fe(NO_3)_3$	hydrogen fluoride Ferrum Nitrate solution
HRTEM	high resolution transmission electron microscopy
HWCVD	hot-wire chemical vapour deposition
ITO	indium tin oxide
$KMnO_4OH$	potassium permanganate solution
L-S	liquid-solid interfaces
MCA	multichannel analyzer
MFC	mass flow controller
NA	numerical aperture of the objective of Raman microscope
NIR	near infrared
PECVD	plasma enhanced chemical vapour deposition
PL	Photoluminescence
RCA	Radio Corporation of America
rf	radio frequency
SAED	selected area electron diffraction
sccm	standard cubic centimeters per minute
SEM	scanning electron microscopy
$SiH_2(C_6H_5)_2$	Diphenylsilane
$SiH_2C_6H_8$	Monophenylsilane
SiH_2Cl_2	Dichlorosilane
SiNPs	silicon nanoparticles
TEM	transmission electron microscopy
TO	transverse optical
UV	Ultraviolet
VLS	vapour-liquid-solid
VS	vapour-solid
V-S	vapour-liquid interfaces
wt%	weight percentage
XRD	X-ray diffraction
YAG	yttrium aluminium garnet
µRS	micro-Raman spectroscopy