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生 年 月 日	
本　　籍	エジプト
学 位 の 種 類	博士(学術)
学 位 記 番 号	博甲第436号
学位授与の日付	平成13年9月28日
学位授与の要件	課程博士(学位規則第4条第1項)
学位授与の題目	FORMATION OF CRYSTALLINE SILICON FILMS HAVING NANOMETER-SIZE GRAINS USING A PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION TECHNIQUE (Plasma-Enhanced化学気相成長法によるナノメーターサイズ粒子をもつ結晶性シリコン膜の形成)
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学 位 論 文 要 旨

ABSTRACT

Recently, increasing interest has been attracted to fabrication and characterization of nanocrystalline silicon (nc-Si), because nc-Si exhibits a quantum size effect and therefore has a potential for application to optoelectronics. In addition, the intensive photoluminescence (PL) at room temperature has attracted much attention for nc-Si films. However, the mechanism of the observed visible PL is still unclear; Some researchers attribute the PL to quantum confinement effects of Si nanocrystallites while others attribute it to silicon-based luminous compounds such as siloxene and polysilane, localized states at the surface of nanocrystallites and amorphous Si. The goal of the present work is to prepare nc-Si films using a plasma-enhanced chemical vapor deposition, and to study their structural and optical properties.

First, the structural properties of nc-Si films deposited at 100°C using $SiF_4/SiH_4/H_2$ gas mixtures were investigated by changing the SiF_4 flow rate ($[SiF_4]$ = 0-0.5 sccm). At a certain low $[SiF_4]$ value (= $[SiF_4]_S$), both the crystallinity (crystalline volume fraction), ρ, and the grain size had minimum values. The Raman peak shifts corresponded well with a change in stress, and films with $[SiF_4]_S$ were suggested to be free from random stress in the local Si-Si networks. The PL spectra had the highest intensity and the highest peak energy at $[SiF_4]_S$.

Second, the correlation between the structural and the optical properties of silicon crystallites formed at deposition temperature, T_d, of 100 and 300°C were studied. As a result, the increase in the PL intensity by decreasing the average grain size, <δ>, was observed at T_d = 300°C. The full-width at half-maximum (FWHM) values of the PL spectra of films deposited at T_d = 100°C were broader than the FWHM values of films prepared at T_d = 300°C.

Third, the structural properties of the nc-Si films were examined by varying the T_d from 95 to 500°C under two different hydrogen flow rates ($[H_2]$ = 0 and 30 sccm). For these films, the x-ray diffraction, the Raman scattering, the Fourier transform infrared absorption and the stress were examined. As a result, it was found that the increase in $[SiF_4]$ under high T_d condition was likely to form preferentially the <110> textured grains along with an increase in the $<\delta(110)>$ but to decrease the $<\delta(111)>$ value. On the other hand, the increase in $[H_2]$ under low T_d conditions caused the enhanced formation of <111> grains acting to increase the crystallinity and to decrease the $<\delta(110)>$ and $<\delta(111)>$ values. Based on these results, a difference in the crystalline properties due to the SiF_4 or H_2 addition under different T_d conditions was interpreted in terms of a difference in the etching rate due to hydrogen and fluorine radicals, depending on the value of T_d. In addition, the etching at an early stage of film growth may cause different surface morphology of the substrate.

Fourth, the optical properties of the nc-Si films were examined by varying the T_d for two different series with two different $[H_2]$: $[H_2]$ = 30 sccm and $[SiF_4]$ =

0.38 sccm as series A films, and with $[H_2]$ = 0 sccm and $[SiF_4]$ = 0.5 sccm as series B films. For these films, two PL spectra were found at around 1.7-1.8 eV and 2.2-2.3 eV. When T_d was increased, it was found that the peak energies, E_{PL}, of the 1.7-1.8-eV PL band for series A films monotonically decreased, in agreement with the increases in the $<\delta(110)>$ values, while those for series B films had a minimum value at around T_d = 200°C, in opposite correlation to the T_d dependence of the $<\delta(111)>$ values. Such a difference between the PL process for series A films and that for series B films was interpreted in terms of a difference in the etching rate due to F-radicals as etchants for Si depending on T_d. The decrease in E_{PL} for series A films with increasing T_d corresponded well with a decrease in the optical band gap, E_g^{opt}.

Fifth, the structural properties in connection with a change in the PL by varying the gas pressure, $[H_2]$, rf power and T_d, were investigated. Nc-Si films exhibited room temperature PL with two peaks at around 1.8 eV (700 nm) and 2.2 - 2.3 eV (540 – 560 nm). The first 1.8-eV-peak is related to a quantum size effect and another peak to the SiH-related bonds. The $<\delta>$ and ρ decreased with decreasing the gas pressure. In contrast, all of the PL peak energy, PL intensity and E_g^{opt} increased. In addition, by increasing $[H_2]$, rf power and T_d, it was found that the values of $<\delta>$, ρ and PL intensity increased and PL peak energy decreased.

Finally, nc-Si films were deposited on fused quartz and single (100) crystal Si substrates using a SiH_4-H_2 mixture at different T_d. The effects of plasma-assisted hydrogenation at 300°C on the optical and structural properties were examined for the nc-Si films. The crystallization of the films was observed at T_d between 500 and 600°C and above 640°C. The film deposited at T_d = 730 °C exhibited PL in its as-deposited state, but the intensity of PL decreased after hydrogenation. Correlation was found between the PL intensity and infrared absorption bands at around 850 and 1000 cm^{-1}.

学位論文審査結果の要旨

各審査委員によって，提出学位論文に関して個別に審査を行うと共に，平成 13 年 8 月 6 日に第 1 回論文審査委員会を開催し，また，平成 13 年 8 月 6 日に開催した口頭発表の結果を踏まえて，同日に第 2 回論文審査委員会を開催して協議を行った。その結果，以下のように判定した。

シリコンナノ結晶粒からなる“結晶性シリコン膜”は，可視光での強いフォトルミネセンス (PL) を示し，発光デバイスへの応用が期待される材料である。本研究では，プラズマ化学気相成長 (PECVD) 法を利用して，原料ガスへの SiF_4 や H_2 のガス流量，および堆積温度を変化させて，その構造学的性質を X 線回折分光，ラマン散乱分光，膜応力，さらにはフーリエ変換赤外分光により構成原子の結合構造を調べている。また，光学吸収や PL などの光学的性質の変化を構造学的性質の変化と関連させて調べている。

Si ナノ結晶における結晶性は，Si 膜堆積中あるいは堆積時初期における，プラズマ中各種ラジカルに起因するエッチングに関連した，様々な効果に強く依存するが，これらの効果が与える影響を分離・解析することは極めて困難である。従って，本研究では，結晶性の変化を，Si に対するエッチャントとしてのフッ素や水素ラジカルの働きの違いに注目して議論している。以上の研究成果は，基礎研究面のみでなく PECVD Si ナノ結晶膜の応用に関する重要な指針を与える。よって，本論文は博士（学術）の学位に値するものと判断する。