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Optical properties of silicon nitride thin films deposited by $TEACO_2$ laser induced chemical vapor deposition

الخواص البصرية لاغشية نتريد السليكون الرقيقة المحضرة بليزر $TEACO_2$ الحاث على ترسيب البخار كيميائياً

Hammad Rahaim Al-Azawi
University of Baghdad, College of Science, Department of Physics
Email- hammad6000@yahoo.com

Abstract

Amorphous silicon nitride thin films were deposited on quartz substrate at temperatures 350^{o}C with deposition rate o.6 nm/pulse by $TEACO_2$ laser induced chemical vapor deposition (LICVD). The reactant gases photo decompose through collision assisted multiple photon dissociate (MPD). The optical properties (absorption spectra, transmittance, absorption coefficient, and optical energy gap) of these amorphous silicon nitride thin films have been characterized, the optical band gap of the films was varied between (1.5-3.0 eV) by changing the reacting gases SiH_4 and NH_3 ratio in reactant chamber. It was seen that the transmission of these films for visible wavelength increase by increasing the content of nitrogen in the films than that for high silicon content.

X-ray photoelectron spectroscopy (XPS) used to determine the composition and purities of the deposited films. The nitrogen content of the films was varied between (16%-57%) where the later represent stoichiometric silicon nitride Si_3N_4. Also from (XPS), these films have high purity and content about 4% oxygen. this high quantity of oxygen attributed to that the amorphous silicon nitride thin films have nanostructure.

الخلاصة

تم تحضير اغشية نتريد السبيكون العشوائية على قواعد من الكوارتز عند درجة حرارة أساس 350^{o}C وبمعدل ترسيب 0.6 nm/pulse باستخدام تقنية $TEACO_2$ ليزر الحاث على ترسيب البخار كيميائياً. حيث يعمل على تفكيك الجزيئات ضوئياً عن طريق التفكك متعدد الفوتونات المعزز بالتصادم.

تم تعين الخواص البصرية (طيف الامتصاص والنفوذية ومعامل الامتصاص وفجوة الطاقة البصرية) لاغشيه نتريد السيكون العشوائي ووجد ان فجوة الطاقة لها تتغير بين (3.0-1.5eV) وذلك عن طريق تغيير نسبة الخلط لغازي السايلين SiH_4 والامونيا NH_3 في حجرة التفاعل. ووجد ان نفوذية هذه الاغشية للاطوال الموجية المرئية تزداد مع ازدياد محتوى النتروجين في الغشاء أكثرمن محتوى السليكون.

استخدمت تقنية طيف الالكترون الضوئي للاشعة السينية (XPS) في تحديد التركيب والنقاوة للاغشية المحضرة واتضح ان محتوى النتروجين في هذه الاغشية يتراوح بين % (16 و 57) وهذه الاخيرة تعادل كمية النتروجين في المركب العياري Si_3N_4 ومن خلال التحليل ايضاً اتضح ان هذه الاغشية عالية النقاوة وتحتوي على كمية من الاوكسجين بحدود 4% وفسر وجود هذه الكمية العالية من الاوكسجين كون الاغشية ذات تركيب نانوي.

Introduction

Amorphous silicon nitride a-SiN is extensively used in the microelectronics industry for a wide variety of applications including use as an oxidation mask, a doping diffusion barrier, the gate dielectric in field effect and thin film transistors, a charge layer in MNOS Metal-Nitride-oxide Semiconductor non volatile memories and as a final passevation layer for device packaging[1]. Silicon nitride thin films are conventionally deposited at high substrate temperature (700-900^{o}C) by thermal chemical vapor deposition (CVD). Due to the increasing complexity of semiconductor processing, several different low temperature deposition methods have been employed in the past for silicon nitride film growth including plasma-enhanced (PECVD) techniques [1,2].

While previous studies of silicon nitride films focused primarily on the electronic and paramagnetic properties of the material, several studies of the optical properties of plasma enhanced chemical vapor deposition (PECVD) silicon nitride films have been made [3,4].

The aim of this project is to deposit SiN thin films with control optical band gap by varying the reactant gas ratio in reactant chamber.

In this work the optical properties of laser induced chemical vapor deposition (LICVD) a-Si_xN_{x-1} films deposited under varying conditions are discussed.

Experiment

A) System design

The laser beam is directed parallel to the quartz substrate, the laser excited the reactant gas without any interaction with the substrate Fig. (1) the gas molecules are directly vibrationally hated by absorption laser energy, and then dissociate and decomposed through collision assisted multiple photon dissociation (MPD) [5].

$TEACO_2$ laser (2J) emitting at a wavelength of λ = 10.6 nm with pulse duration 100 ns peak power about 20MW . The beam shaped to have square cross section (3cm×3cm). Reactor pressure are maintained in the range of 400 mbar, reactant gases NH_3 and SiH_4 are mixed in reacting chamber with different ratio. Films were deposited on quartz substrates with deposition rates 0.6 nm/pulse and thickness of (600±25 nm) to promote uniform film the substrate in all cases, is fixed at 350^oC by using resistively heated element and controller. Films were deposited under variety of condition to have variety SiN films with variety silicon content as summarized in Table (1).

Table (1)

NH_3/SiH_4	NH_3 Pressure (mbar)	SiH_4 Pressure (mbar)
1/1	200	200
3/1	300	100
12/1	370	30

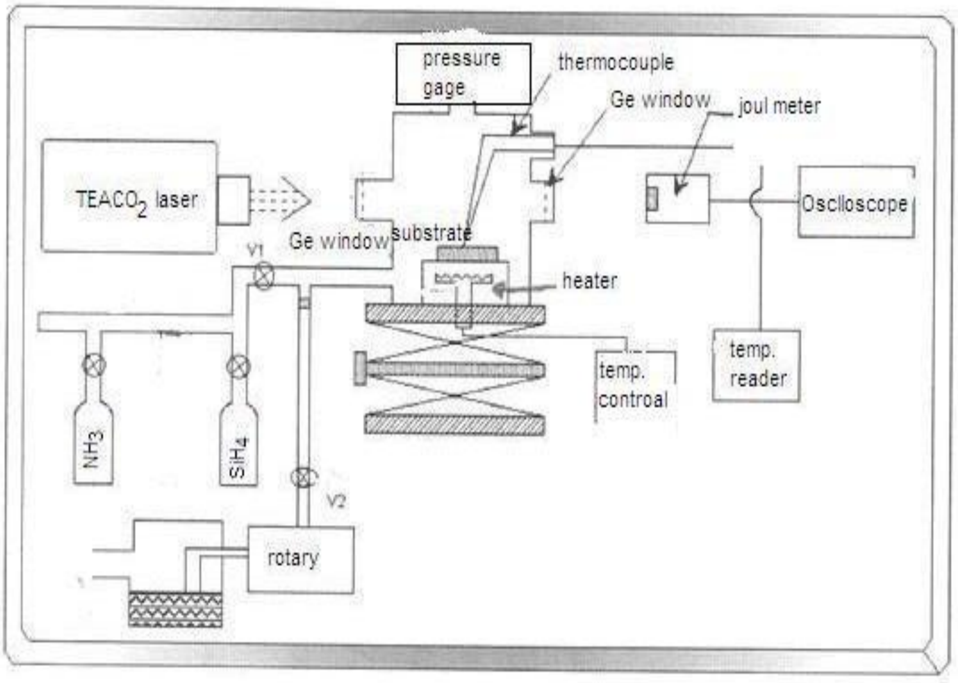

Fig. (1): Schematic side view of the laser induced chemical vapor deposition (LICVD) set-up configuration

B) Analytical methods

The dense films have been characterized with several spectroscopic and analytical methods X-ray photoelectron spectroscopy (XPS) measurements which determined the stoichiometry of the films and its impurities, as a function of deposition conditions. X-ray diffraction for structural properties, scanning electron microscope (SEM) for thickness measurements were carried out. UV-VISIBLE spectrophotometer in the range (300-1100 nm) for optical properties (optical band gap and absorption constant) were calculated.

Results and Discussion

A) Composition and purities

To determine the composition of the films XPS, analysis has been performed. The composition of the three thin films with formula $Si_{0.84}N_{0.16}$, $Si_{0.59}N_{0.41}$, $Si_{0.43}N_{0.57}$ are determined. The latest one represents stoichiometric silicon nitride Si_3N_4, where Si% equal to 43% and N% equal to 57%.

From (XPS) Fig. (2) there is no impurities detected except 4% oxygen, which determined from the peak centered at (531 eV). The main contamination with oxygen occur after deposition, when the sample are exposed to ambient air, so we believe that the films have nanostructures, so it have large surface to volume ratio [6].

The two peaks at 397 eV and 403 eV represent N_{1S} these two peaks indicate that nitrogen is bonded to silicon and oxygen. Where the first peak represents Si- N bonding energy and the second peak represents N - O bonding energy. Where the peak at 100eV represents the binding energy for Si_{2p} and the peak at 150eV represents the binding energy for Si_{1s}.

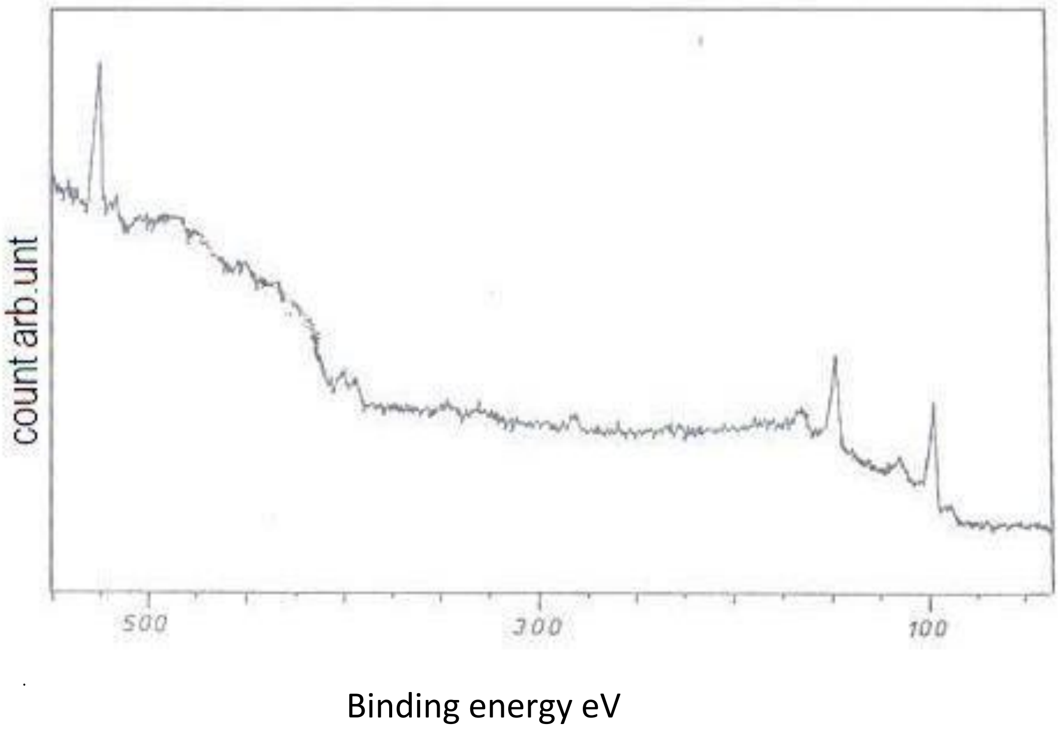

Fig. (2): X-ray photoelectron spectroscopy for the $Si_{0.84}N_{0.16}$ thin film.

B) Structural properties

From X-ray diffraction patterns of the Si_xN_{1-x}, it was found all studied thin films were amorphous and Fig. (3) shows the X-ray diffraction pattern for one of these films and all the amorphous films have the same X-ray diffraction pattern. These films have amorphous structure because they deposit by short pulse laser so that the reaction time is very short and there is no more time for deposited films to have crystalline structure.

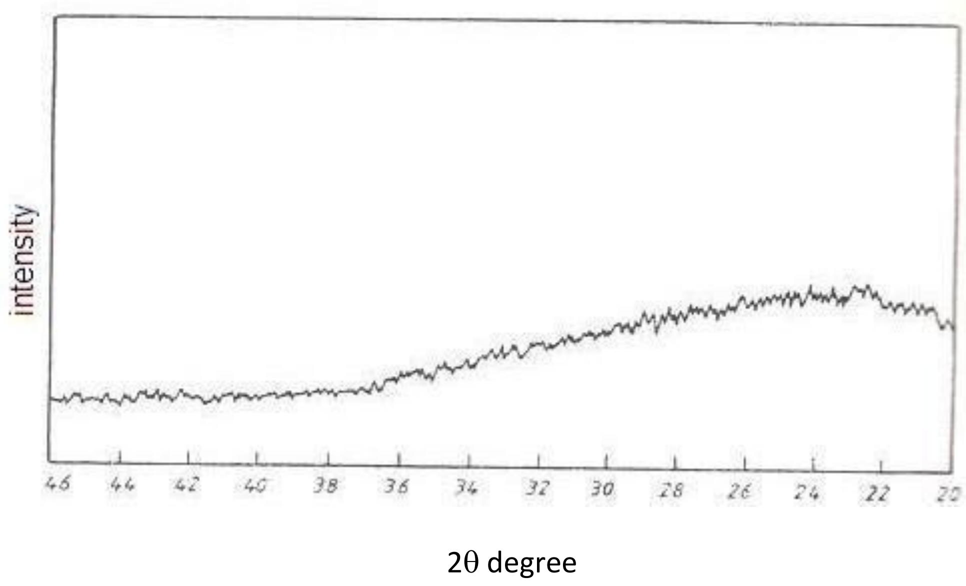

Fig. (3): The X-ray diffraction patterns

C) Optical properties

Transmission spectra of the films were taken from near ultraviolet 300 nm to near infrared 1100 nm. The variation of the absorption coefficient (α) versus the wavelength of the deposited thin films was shown in Fig.(4). The absorption coefficient (α) given by

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d} ------------(1)$$

where T: Transmission

and d: films thickness.

From the figure we show that the films have high light transmission in the visible region and this transmission increased with increasing the nitrogen content.

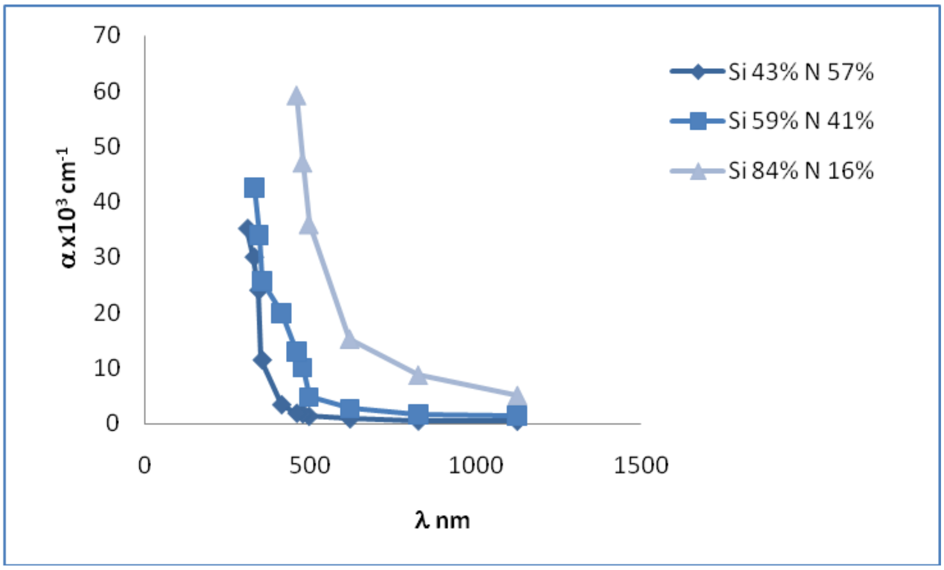

Fig. (4): Absorption coefficient (α) as function of wavelength for the silicon nitride thin films.

The optical band gap was calculated using Tauc relationship which given by the formula [7]

$$\alpha h\nu = A(h\nu - E_{op})^{n} ---------(2)$$

where hν is photon energy,
E_{op} is the optical band gap material.
A is constant
n=2 for indirect band gap material.

When $(\alpha h\nu)^{1/2}$ is plotted as a function of hν the curve is extrapolated to $(\alpha h\nu)^{1/2}=0$. The band gap of the Si_xN_{1-x} thin films as deposited found from Fig. (5). It was seen that the band gap for $Si_{0.84}N_{0.16}$, was 1.5 eV, for $Si_{0.59}N_{0.41}$ was 2.6eV and for $S_{i0.43}N_{0.57}$ was 3 eV. Where film with 84% Si content's is near for Si, it has optical band gap near the band gap for Si thin film. And when nitrogen content is increased the film become near Si_3N_4 thin film than for Si so the optical band gap is increased, where Si_3N_4 has high optical band gap than Si.

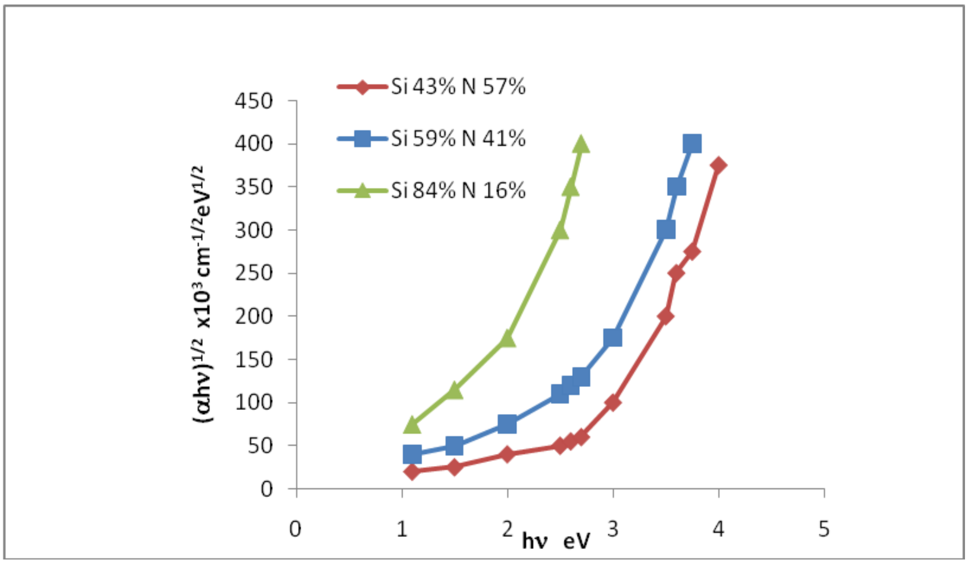

Fig. (5): A plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy for silicon nitride thin films.

The optical band gap could be reproducibly varied by changing the reacting gas ratio. We show from Fig.(6) that the optical band gap increased by increasing the nitrogen content in the films. This result is comparable to that found by other [8] where deposited silicon nitride films by hot filament assisted chemical vapor deposition (HFCVD).

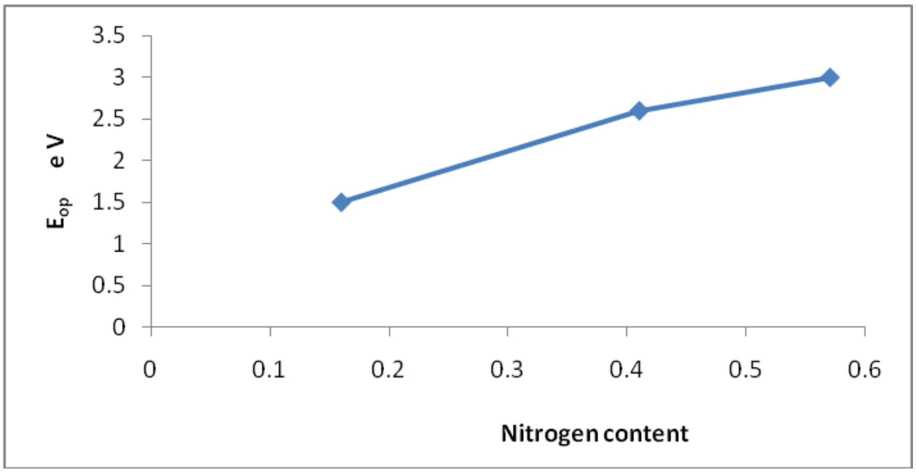

Fig. (6): Energy band gab as function of nitrogen content for the silicon nitride thin films.

Conclusions

This article presents the optical properties and purity of a series of silicon nitride films deposited by laser induced chemical vapor deposition method. The optical band gap can be controlled by varying the film stoichiometry, which is a function of reactant gases ratio.

The films contaminate by high quantity of oxygen after deposition, when the films are exposed to ambient air, so we conclude that the films have nanostructure. The films have no other contamination material like carbon.

It is not possible to deposit silicon nitride films with nitrogen content higher than that in Si_3N_4 and that attributed to the nitrogen gas nature.

Stoichiometric silicon nitride films have higher transparent in visible region than that have high silicon content.

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