HIGHLY ORIENTED DOPED AND UNDOPED TIN OXIDE THIN FILMS GROWN ON MULTICRYSTALLINE SILICON SUBSTRATE

Reçu le 26 Décembre 2007 – Accepté le 25 Avril 2009

Résumé

Des couches minces d'oxyde d'étain polycristallin pure et dopé avec différentes concentrations de dopant ont été déposés sur du silicium multicristallin. Pour une étude comparative sur leur croissance et leur caractérisation des substrats de verre ont également été utilisés. Les résultats de la diffraction RX, nous ont montré une croissance préférentielle selon le type de substrat. Sur les substrats de verre la croissance des grains se fait suivant les orientations cristallographiques (101, 211, 200..) alors que sur les substrats de silicium polycristallin la croissance se fait suivant les directions (110, 211, 101…). La microstructure des films obtenus est colonnaire avec une taille de l'ordre de 200nm. Pour les mêmes conditions de préparation (440°C pour la température du substrat, 10mn pour la durée de dépôt et 2L/mn pour le flux d'oxygène), la résistance surfacique mesurée sur les couches dopées est améliorée, comparée à celle mesurée sur des films non dopés. Contrairement à des résultats obtenus sur des couches de SnO_2 déposées sur du silicium monocristallin, la microstructure semble être dépendante du type de substrat.

Mots clés *: Dopage, Propriétés structurales, Diffraction RX*

Abstract

Polycrystalline antimony doped and undoped tin oxide thin films are grown by chemical vapor deposition on multicrystalline silicon and on glass substrates. The latter substrate was considered for comparative study on growth and characterization. The doping was achieved with various content of Sb in the starting material. X ray diffraction patterns let us to find preferential growth which is not the same according to the substrate. On the glass substrate the grain grows in the (101, 211, 200) crystallographic direction while it grows in the (110, 211, 101) orientation when deposited on polycrystalline silicon substrate at the same time and in the same reactor. The resultant films possess a columnar microstructure perpendicular to the substrate and exhibits grains with nanometer size. The sheet resistance measured on doped layers are significantly improved compared to that obtained on undoped ones, in the same conditions i.e. substrate temperature Ts=440°C, duration of the deposition 10 min and flowing oxygen about 2L/min. Contrary to results obtained on tin oxide layer deposited on monocrystalline silicon in previous work the microstructure seems to be dependant on the kind of the substrate.

Keys words *: Doping, structural properties, diffractogram*

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ملخص

شـــرائح رقيقة متعددة البلورات من مركب ثنائي أكسيد الإيثان المشوب بالأنتموان والغير المشوب زرعت فوق دعامات من السيليسيوم متعدد البلورات وأخرى من الزجاج بإستعمال تقنية "وضع البخار كيميائيا" الدعامات الأخيرة أستعملت من أجل الدراسة المقارنة للبنية والخصائص. الإشابة تمت بكميات متفاوتة من الأنتموان بالنسبة لثاني أكسيد الإيثان . إنعراج الأُشعة السينية سمحت لنا بإيجاد وضعية الترسب المفضلة المتغيرة بحسب طبيعة الدعامة. تم ترسيب الحبيبات في الإتجاهات البلورية (101, 211 , 200) بالنسبة للدعائم الزجاجية, بينما تم في الإتجاهات (110, 211, 101) فوق دعائم السيليسيوم متعدد البلورات. البنية الدقيقة للطبقات الناتجة عبارة عن أعمدة أهرام عمودية على الدعامة وبحبيبات من رتبة النانو متر. المقاومة السطحية المقاسة بالنسبة للطبقات المشابة تختلف إختلاف معتبرا عن تلك الخاصة بالطبقات غير المشابة المتحصل عليها في نفس الشروط التجريبية : درجة حرارة الدعامة : 440°C زمن الوضع : 10د تدفق الأكسجين : 2ل /د. على عكس النتائج المتحصل عليها في عمل سابق بالنسبة لطبقات ثنائي أكسيد الإيثان المبخرة فوق السيليسيوم احادي البلورة : يلاحظ أن البنية الدقيقة تتأثر بنوع الدعامة يتمثل هذا العـمل في تحـــليل عدم الاستـقرار مرونة انبعاج الصـــفائح المـصففة ذات التشويه الهنـدسي. الانبعاج الصـــفائح ذات المـــواد المركـــبة و هي ظـــاهرة معقـدة جـــدا. لتحمـيل الانبعاج الصفائح الرقـيقة المصـففة قمنـا باستخــدام عنـصر متكون من أربـــع عقـــد و 32 درجة متـحررة، العـلاقة المعـتمدة عـــلى نظرية **(كرشوف)** و الـــتي تتمثل في أحـــادي الطـبق المكـافئة لطبقـات الصـــفائح المصـــففة. ثم قمنـــا بتقديم مشـــاكل صياغة عـــدم الاستـقرار باستعمـــالنا مبـدأ تغـــير الثـــــاني للطـــاقة الكـــامنة في بنـــاء صلابة المـصفوفات. قمنـــا بتجـــارب عـــدة عينـــات لظـــاهرة الانبعاج الصفـــائح الرقيـــقة المتـــجانسة و غـــير المتـــجانسة (مركبة) و النتـــائج المتحـصل عليهـــا مقـــارنة مـــع النتـــائج المرجعـــية المـــتوفرة أثبتـت تقـــارب النـــتائج و نجـــاعة العنـــصر المستـــخدم. ثـــم ثقـــب الصفـــحة و الـــمركبة عـــدة مرات وبينت النتـــائج أن الحـــمولة الحدية لانبعاج تـــزداد مـــع زيـــادة مســـاحة ثقـــب مـــربع الشكـــل و ذلك مـــع بعـض الـــشروط الحـــدية.

الكلمات المفتاحية *: إنعراج الأشعة السينية الإشابة*

Tin oxide films have been the object of many studies. For amorphous silicon solar cells, SnO_2 has been widely used as a front transparent conductive oxide (TCO) layer due to its controllability of surface morphology as well as good light trapping performance and its lower cost.

In general, the semiconductor oxide gas sensors like SnO_2, have been widely studied due to their range of conductance variability and their response towards both the oxidizing and reducing gases. Only few studies have been examined for the optimum design of substrate texture to realize further improvement of the photovoltaic performances of poly-Si solar cells.

In this work, the goal is the study of the influence of polycrystalline silicon substrate on the microstructure of pure and doped tin oxide film because the substrate surface morphology plays a dominant role in the preferential growth of TCO layer. In order to investigate the influence of substrate texture on SnO_2-Sb microstructure, we performed XRD measurements for the SnO_2-Sb films deposited by a home developed CVD method, on glass and multicrystalline silicon substrates.

In this work, a series of pure and antimony doped tin oxide Sb-SnO_2 have been fabricated by APCVD on glass and polycrystalline silicon substrates with different contents of antimony atoms and investigated concerning the influence of substrate on microstructure. In previous work on tin oxide [TSF], the Sb dopant ratio was varied between 0% and 4%.

The variations, on some properties as resistivity, transmittance, were significant only in the range of 0.7 to 1.6%. So in this work we will present results in the latter range.

1. EXPERIMENTAL DETAIL

For preparation of tin oxide films, the starting material was a gas phase mixture of ($5H_2O$, $SnC1_2$), pure oxygen and an amount of antimony trichloride (SbCl3). Different amounts of $SbCl_3$ were added to the quantity of hydrated $SnCl_2$ to obtain the final antimony doped films.

The Sb/Sn ratio was varied over a range of 0.7% to 1.3%. The substrates to be deposited were first cleaned by organic solvents and then rinsed with double distilled water. The as prepared films were structurally characterized. The scanning angle 2θ was varied from 2° to 90° in step of 0.05°. In order to study the optimal deposition temperature, pure SnO_2 layers were first deposited at the same time on optical grade microslide with an effective area of 1.0 cm×2.5 cm and poly-c silicon at different temperatures.

The substrate temperature was varied between 350 and 450 ◦C. The deposited time was maintained at 10 min. Compressed oxygen with a flow rate of 2 l min^{-1} was used as oxidant agent and as a carrier gas.

2. Results and discussion

Since change in the antimony doping can be correlated with the variations in the electrical and optical properties of Sb doped tin oxide layers deposited on glass substrates [TSF], XRD measurements were made to determine the correlation and the influence of the Sb doping on crystallographic structure and grain size of the crystallites of Sb-SnO_2 films deposited on both glass and poly-c silicon substrates.

However this study is also focused on poly-c silicon substrate influence on structural properties. Typical X-ray diffraction spectra recorded on SnO_2 films deposited on poly-c silicon substrate at several temperatures are shown in Fig.1. All the diffractograms contain the characteristic tin oxide peaks. The XRD patterns were indexed on the basis of a tetragonal structure with the lattice parameters a = 4.804Å and c = 3.079 Å.

The peaks observed are (110), (211), (101) and (200) at 2θ=38°. The (110) peak is the strongest one for all the films and the great intensities are observed for the temperature of 443°C. From these results we can conclude that the substrate temperature does not affect the preferred (110) orientational growth of the films but affect the intensity of this peak.

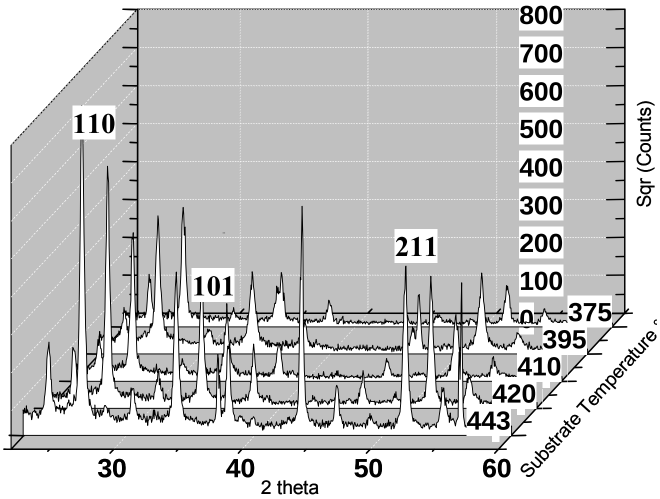

Figure 1 : X-Ray diffraction spectra of SnO_2 layer deposited on poly-c silicon. Influence of substrate temperature.

Therefore, our doped films were deposited at a substrate temperature of 440° C with a deposition time of 10 minutes. Some results on electrical and optical properties of our films doped and pure have been previously reported in a previous work [TSF].

In the following work we will examine structural details derived from XRD measurements of the deposited films on polycristalline silicon in connection with the structural properties on glass substrates by varying the antimony doping level.

The antimony content (in percentage of doping atoms) in each doped film was determined from the following expression :

$$S_b / S_n = \left(\frac{n\,\text{atoms}\,S_b}{n\,\text{atoms}\,S_n} \right) \% \qquad (1)$$

At first we have investigated the influence of incidence angle on XRD diffractograms. The diffraction patterns X recorded at different incidence angle of the X-ray incident beam let us to find optimal incidence angle.

The results of this investigation are shown in figure 2. It appears clearly that the best angle is 0.5°. In the following XRD spectra are recorded at this angle.

The preferred orientation of the SnO_2-Sb films deposited on poly-c silicon was calculated by the texture coefficient C_T of the hkl plane from equation 2 [1] given in follow.

$$C_T(hkl) = \frac{I(hkl)/I_0(hkl)}{\left(1/N\right)\sum_n I(hkl)/I_0(hkl)} \qquad (2)$$

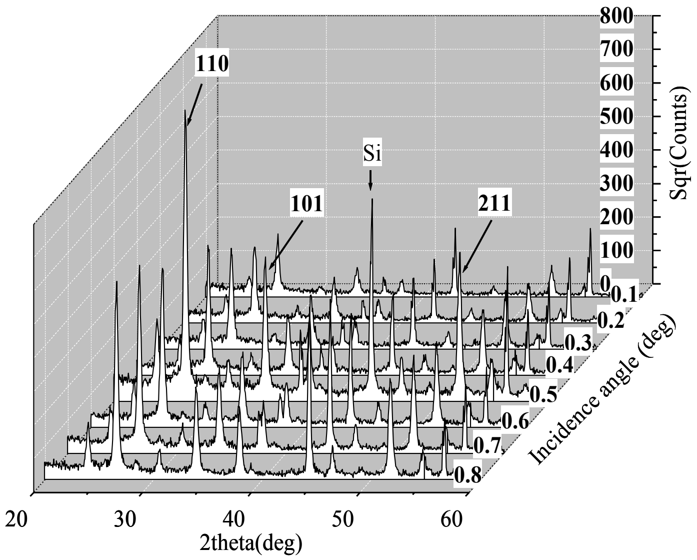

Figure 2 : Influence of incidence angle on preferential orientation

Where *I(hkl)* the measured and I_0 *(hkl)* the corresponding standard intensity given by the ASTM cards of cassiterite. Figure 3, show the ratio of (110) and (hkl) diffraction intensities, which gives a clear indication of a degree of (110) preferential orientation for S_b/S_n about 0.85 %.

Figure 4 shows the XRD profile of the non doped and antimony-doped tin oxide films deposited at temperatures 440 °C. The antimony doping level is the same and it is about 0.85%.

The reflections from the tetragonal crystallographic pattern of either pure or doped tin oxide deposited on glass substrate become more intense and sharp. The addition of dopants results in the change of preferred (101) orientational growth of the films which now exhibits the (110) preferential orientation.

The most striking feature from the XRD results is that the substrate does not affect the preferential orientation peak but it affect his intensity.

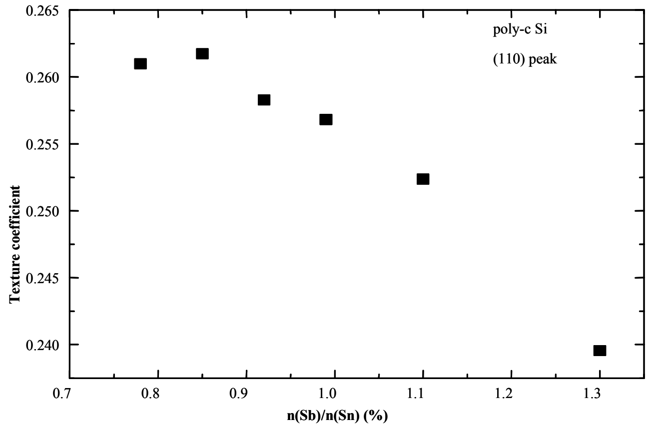

Figure 3 : Texture coefficient C_T of the 110 plane as a function of antimony doping level

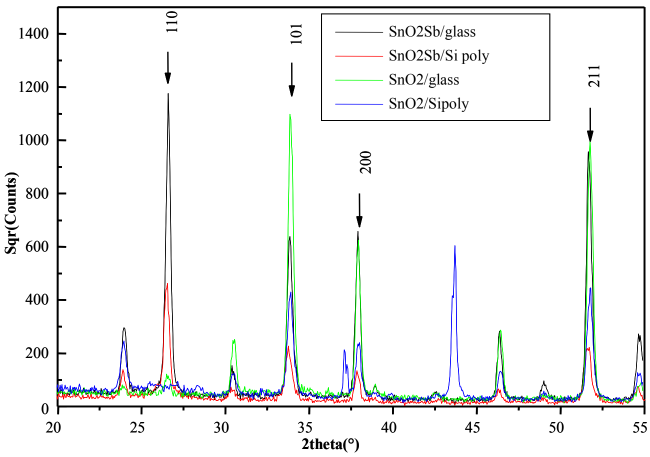

Figure 4 : Influence of the substrate on X-Ray diffractograms

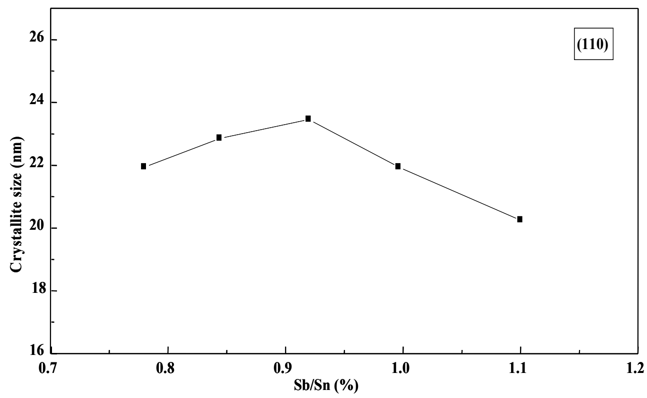

Figure 5 : Variation of crystallite size with dopant ratio for films deposited on poly-c silicon substrate

The crystallite size calculated from the Scherrer formula for antimony-incorporated tin oxide thin film is between 20nm and 24nm. The results are given by the figure 5.

CONCLUSION

SnO_2 either doped or undoped are deposited on glass and multicrystalline silicon substrates.

Tin oxide crystallize in a tetragonal system. At Sb content about 0.85%, the 110 peaks become more intense when for non doped films 101 is the preferential orientation growth. Polycrystalline silicon substrate have a significant effect on the structural properties of tin oxide films either doped or undoped, hence structure coefficient and the grain size measurements of the crystallites were carried out.

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Acknowledgements

We wish to thank Layachi (CDTA) for his contribution to X-Ray measurements.