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Spectroscopic ellipsometry study of nickel induced crystallization of a-Si

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Abstract

The aim of this work is to present a spectroscopic ellipsometry study focused on the annealing time effect on nickel metal induced crystallization of amorphous silicon thin films. For this purpose silicon layers with 80 and 125 nm were used on the top of which a 0.5 nm Ni thick layer was deposited. The ellipsometry simulation using a Bruggemann Effective Medium Approximation shows that films with 80 nm reach a crystalline fraction of 72% after 1 h annealing, appearing to be full crystallized after 2 h. No significant structural improvement is detected for longer annealing times. On the 125 nm samples the crystalline volume fraction after 1 h is only around 7%, requiring 5 h to get a similar crystalline fraction than the one achieved with the thinner film. This means that the time required for full crystallization will be strongly determined by the Si layer thickness. Using a new fitting approach the Ni content within the films was also determined by SE and related to the silicon film thickness.

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1. Introduction

The polycrystalline silicon (poly-Si) processing temperature has been forced to decrease due to the constant demanding for low cost devices and consequent use of low cost substrates such as commercial glass. Thus, instead to produce poly-Si by direct deposition, it has been obtained by crystallization of amorphous silicon (a-Si), using either laser or thermal annealing [1,2]. Metal induced crystallization (MIC) emerged as an effective crystallization technique, overcoming some problems associated with other crystallization techniques, being non-expensive and presenting good uniformity over large areas. Nickel (Ni), is known to dissolve in the a-Si weakening Si bonds and enhancing the nucleation of crystalline silicon at temperatures lower than 500 °C [3], a value below than its intrinsic crystallization temperature (~600 °C). The reaction occurs at the interlayer by diffusion and the driving force for the crystallization is the difference on the free energy between amorphous and crystalline phases. During the initial stages of the MIC process, a silicide ($NiSi_2$) layer is formed at the a-Si/Ni interface. After that this layer breaks-up in small nodules and these nodules start migrating through the a-Si, leaving behind crystallized silicon. The diffusion velocity of the silicide nodules will depend on their size, with the small ones moving faster than the largest ones [4]. As this is a diffusion/surface reaction controlled process [5], the annealing time will be a critical parameter in determining the final properties of the crystallized layer, being dependent not only of the temperature but also of the metal/silicon ratio [6]. However, one critical limitation of MIC is the device's performance degradation due to the imbedded metal impurities (surface and bulk contamination). Most metals form deep dopants or act as recombination centers

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[7]. This is controlled by metal diffusion and solubility and it is related with the metal thickness deposited on the a-Si. Spectroscopic ellipsometry (SE) has proved to be effective in characterizing poly-Si layers [8] and also in determining their crystalline fraction [9–11]. When using a new approach to the simulation procedure, SE reveals also some potentiality in determining the Ni concentration within films after crystallization. That is why SE may be a powerful tool in controlling the crystallization process and it is imperative to see how it is sensitive to changes on some process parameters, the aim of the present paper.

2. Experimental details

The a-Si samples with 80 and 125 nm were deposited in a tubular LPCVD Tempress Omega Junior furnace on glass (Corning 1737) at 550 °C, 30 Pa and with a silane (SiH_4) flow of 30 sccm. Before the metal deposition the samples were cleaned in buffered fluorohydric acid for 20 s in order to remove the native oxide and after that they were washed in de-ionized water. Ni layers with and 0.5 nm were deposited over the a-Si samples by e-beam evaporation. The samples were then annealed, respectively, for 1, 2, 5 and 10 h at 500 °C in vacuum, under an inert gas atmosphere. The structural properties were evaluated by spectroscopic ellipsometry (SE) and X-ray diffraction (XRD). The crystalline volume fraction was determined from SE data using a Bruggemann Effective Medium Approximation (BEMA) [12]. The simulation model is constituted by four layers. Since the glass substrate is transparent it is imperative to take into account the back interface between the glass and the air. So, the first layer simulates the environment using voids as reference. The second layer is a dispersion formula that simulates the optical response of the glass. The third one is a BEMA layer that simulates the bulk and it is formed by a mixture of a-Si, poly-Si and Ni. The last one is also a BEMA layer that simulates the roughness, being formed by 50% of silicon oxide (SiO_2) and 50% of voids. The fitting was done using the I_S and I_C parameters, that are related with the reflection angles Δ and Ψ. However, in this analysis it is presented the dielectric function in order to provide a better understanding of the SE results. Rutherford backscattering spectroscopy (RBS) measurements were done to analyze the Ni depth profile inside the full crystallized poly-Si layers and these data correlated with the ones obtained from SE.

3. Results

The RBS data (Fig. 1) for totally crystallized Si samples with 80 and 125 nm show the presence of a non-uniform Ni distribution, where two concentration peaks are visible. Integrating the overall area, similar values were obtained for all samples, confirming that the initial Ni layer thickness was equal. Calculating the channel difference on the surface and at the end of Ni diffusion zone, it is approximately obtained 729–679 = 50, for the 80 nm samples

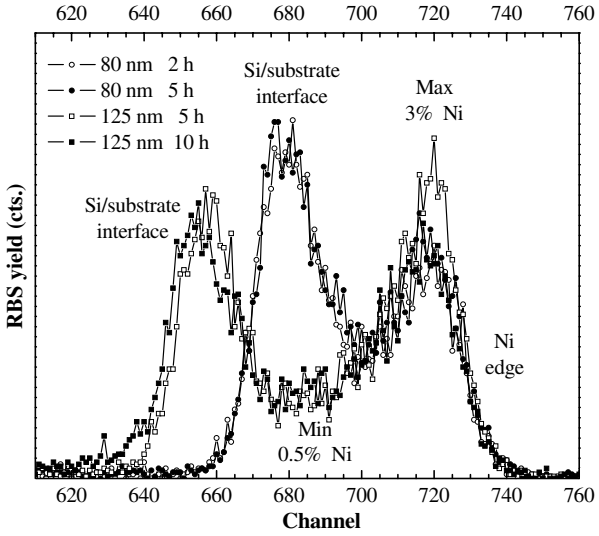

Fig. 1. Ni depth profile obtained by RBS. Two metal accumulation regions appear one at the surface and other at the silicon/substrate interface.

and 729–657 = 72, for the 125 nm samples. The ratio between them is 0.69, which is close to the ratio between the sample's thickness (80 nm/125 nm = 0.64), confirming so that the Ni accumulation zones are located at the surface and at the substrate/silicon interface. The accumulation region at the substrate/film interface is attributed to the fast moving $NiSi_2$ silicides that reach the bottom interface during the annealing and that are responsible by the crystallization process [4]. The Ni concentrations within the film and at the surface's edge can be related either with slower diffused silicides or with Ni itself [5]. The maximum metal concentration inside the films was around 3%, obtained at the film's edges. It has a minimum around 0.5%, inside the 125 nm films, being a little higher on the 80 nm thick films.

The Ni concentration determined by RBS within fully crystallized films are a reference concerning the SE results. This allows improving the SE fittings by introducing the metal as a constituent of the BEMA that is used on the simulation of the film's bulk. Due to software package limitations, only three different constituents may be used in each BEMA layer, which means that one of them had to be replaced by Ni. On crystallized samples some a-Si will always remain on non-crystallized areas, and the presence of it on the BEMA is always necessary. The use of poly-Si as reference it is also needed and as it takes already into account the grain boundaries (typically voids regions), in this approach voids are replaced by Ni on the BEMA model.

However, despite presenting a non-uniform distribution within the crystallized films, on the SE fitting it was assumed a constant Ni concentration. The accumulation regions detected by RBS can be related with the presence of $NiSi_2$ instead of free Ni and so, to avoid a complex ellipsometric model, a constant concentration was assumed.