Proceedings of the 1st IEEE International
Conference on Nano/Micro Engineered and Molecular Systems
January 18 - 21, 2006, Zhuhai, China

Kinetics of Solid Phase Epitaxy of Amorphous Si Induced by Self-ion Implantation into Si with Nanocavities

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***Abstract*—The solid phase epitaxial regrowth of structurally modified amorphous silicon created by self-ion implantation into nanovoided crystalline silicon is investigated. It is demonstrated that although the modified amorphous silicon is fully reconstructed into single crystal during the epitaxial regrowth, both activation energy and atom attempt frequency for the regrowth are much higher than those of the typical amorphous Si induced by self-ion implantation into Si wafer without nanovoids. The novel regrowth kinetics indicates that the modified amorphous silicon would contain a very high concentration of dangling bonds, which are believed to result from dissociation of the nanovoids originally metastablized in crystalline silicon. The unparalleled sensitivity of SPEG provides an effective and simple way to detect and characterize the subtle structural changes at nanometer scale in amorphous Si.**

Keywords—solid phase epitaxial regrowth; less dense amorphous silicon; crystalline silicon; self-ion implantation; nanocavities

I. INTRODUCTION

Thermally activated solid phase epitaxial growth (SPEG) of amorphous semiconductor surface layer into its single-crystal substrate was first reported by Mayer et al. in 1968 [1]. It has been investigated for last thirty years [2] because of its particular technological importance in integrated circuit technology and its sensitivity to subtle structural and compositional change in amorphous semiconductors. In fact, SPEG is a special kind of first order phase transformation process of a nonequilibrium, discontinuous, and diffussionless nature. During SPEG, the single crystal substrate on which amorphous layer continuous to surface lies can serve as pre-existing, artificial nucleating "seed". This seed can be construed to be of two dimensions with indefinitely large diameter. During SPEG, front transforming crystalline-amorphous (c/a) interface is maintained planar and area of the interface is kept at a constant value throughout its moving toward free wafer surface. Thus, there is no extra energy barrier to be overcome to balance the increase in phase interface energy or deformation energy induced by misfit-strain as occurs during random (heterogeneous) nucleation and growth (RNG) with isolated nucleating "seed". Also due to this epitaxy growth manner, SPEG has neither complicated by long distance atom diffusion nor by variation in local atomic arrangement at the interface caused by the irregularity of the curved interface of the isolated nucleating "seed" during RNG process [3]. Thus, rate of SPEG simply depends on temperature by Arrhenius relation $v=v_0\exp(-E_a/kT)$. In the relation, the single preexponential factor v_0 and the single activation energy E_a have clear physical meanings, respectively straightforward standing for the attempt frequency and the energy barrier for the atoms to jump from amorphous layer to crystalline layer at the planar transforming c/a interface. In addition, such an epitaxy, moving interface can be easily monitored in an *in-situ* and real time manner by a time- resolved optical reflectivity (TRR) technique as first developed by G. L Olson et al. [4]. Therefore, SPEG potentially provides us a unique, sensitive tool to study kinetic transiting process for atoms in amorphous phase to rearrange in a layer by layer manner into single crystalline phase .

Silicon is the archetype elemental semiconductor system for studies of SPEG. Numerous experiments have shown that amorphous silicon (a-Si) layers induced by self-ion implantation at low temperatures, where implanted defects are essentially immobile, most closely approximate the structurally intrinsic state of a-Si [5] (here we call it "structurally intrinsic" so as to distinguish it from the so-called "compositionally intrinsic"). Thus, the kinetics of SPEG of the so-created a-Si layers is believed to be representative of the "intrinsic" kinetics of the SPEG. For a-Si layers on Si (100) induced by self-ion implantation deep enough into wafer surface where H effect is avoided, rate of moving c/a interface during SPEG follows Arrhenius relation with an activation energy of 2.70±0.02eV and a preexponential factor of around 4.64×10^{-8} cm/s [6]. It is widely believed that these are the most accurate kinetic parameters available for describing SPEG of the structurally intrinsic a-Si.

However, the intrinsic a-Si would be an ideal state of homogeneous morphology with a volume expansion not larger than 1.8% with respect to crystalline Si (c-Si). More specifically, the intrinsic a-Si would contain no vacancies or dangling bonds and would be homogeneous on nanometer length scale [7], which can be described by continuous random network (CRN) model. This structure would only exist at temperature of absolute zero degree. The morphology and structure of an actual amorphous solid at temperatures above absolute zero degree, however, more or less contains vacancies or dangling bonds because formation energy of vacancy in a-Si can never be indefinitely large. Depending on method of preparation and thermal history of sample, as do many other properties [7], a real a-Si structure always more or less deviates from the intrinsic one. For instance, density deficit of amorphous silicon structure can be very variable, sometimes going above 10% with respect to c-Si as normally found in deposition on a cold substrate. Such "defected" amorphous structures are difficult to be characterized by TEM

The financial support from the National Natural Science Foundation of China under Grant Nos 90401022 and 90406024, the Science and Technology Key Project of Education Ministry of China under Grant No 105099, and the Faculty Startup Fund at Xiamen University under Grant No XK0012 is acknowledged.

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or other microanalysis techniques. This is especially true when the formation of nm-sized voids (nanovoids) or clustering of dangling bonds in a-Si are highly localized in nm-sized regions, which may or may not be connected [8], losing the CRN pattern of the structurally intrinsic a-Si. Because of increasing technological importance and theoretical interest in this kind of modified amorphous structure, it is very urgent to find a feasible technique to detect and characterize such a structure.

For the above considerations, in this paper, a highly localized, structurally modified amorphous Si layer was for the first time created by a self-ion implantation into a crystalline Si wafer containing a very narrow band of nanocavities. We then studied the kinetics of SPEG of the modified amorphous Si layer via an *in-situ* TRR observation and measurement combined with microanalysis via several other ex-situ techniques. It was demonstrated that although such an amorphous structure was fully reconstructed into single crystal during SPEG, both activation energy and atom attempt frequency for the regrowth are higher than those of structurally intrinsic amorphous Si. Such changes in kinetics indicates that the structurally modified amorphous silicon would contain much higher concentration of dangling bonds and thus would be much less dense than structurally intrinsic amorphous silicon. The study also demonstrated that the established TRR measurement of SPEG is uniquely sensitive and can provide an effective and simple way to detect and characterize the nanosized, less dense layer structure in amorphous Si.

II. EXPERIMENTAL

A buried band (about 200 nm wide) of nanocavities, located at about 550 nm from surface of a Cz Si wafer (n-type, 5-10 cm) of (100) orientation as shown in Fig.1(a), was introduced by an implantation of 50 keV H ions to a dose of $3x10^{16}$ cm^{-2} at room temperature followed by an annealing at 850 ^{o}C for 1 h. An amorphous Si layer of about 1μm in thickness from wafer surface as shown in Fig.1(b) which overlaps the original cavity band region was created by Si ion self-implantation at three energies (70keV to a dose $1x10^{15}$ cm^{-2}, 330 keV to a dose $3x10^{15}cm^{-2}$, and 700keV to a dose $5x10^{15}cm^{-2}$) at liquid nitrogen temperature. To avoid ion channelling effects, all the implanted samples were titled ~ 7° from the incident beam direction. The base pressure during implantation was lower than $5x10^{-7}$ Torr. The a-Si layer was then recrystallized at different temperatures on an *in situ* TRR setup with a 1523 nm laser [9]. To detect any possible remained nanovoids after the amorphization and subsequent recrystallization, Au was introduced, using an 80 keV Au implant to a dose of $4x10^{14}$ cm^{-2} at room temperature into the near-surface of both the c-Si sample containing cavities and the sample containing cavities that had been subsequently amorphized and then crystallized. A furnace anneal at 850 ^{o}C for 1 h in an argon gas flow was then performed to detect cavities [10] and residual open volume defects [11] in both cases.

The amorphous layer thickness and structure, the H-implanted damage profile, the crystal quality, and any movement of Au to cavities were determined with Rutherford backscattering and channeling (RBS-C) using 2.0MeV He ions. The microstructure was examined by cross-sectional transmission electron microscopy (XTEM) using a Philips 430 microscope operating at 300keV. The detailed TEM analysis[12] (micrograph not shown here) shows that the induced nanocavities in the band as shown in Fig.1 (a) has a Gaussian size distribution with diameters from 1 to 25nm and with an average distance of ~ 25nm separating them.

III. RESULTS AND DISCUSSION

The XTEM micrograph (Fig.1 (b)) after implantation shows a featureless amorphous layer (~ 1μm) continuous to surface induced by the above multiple implant, even in the region where the original cavities were present. Our *ex-situ* [13] and *in-situ* [14] observations demonstrate that the nanocavities shrunk along with a preferential amorphization [15,16] at cavity sites during the self-ion implantation. The shrunk cavities were supposed to dissolute into the a-Si as

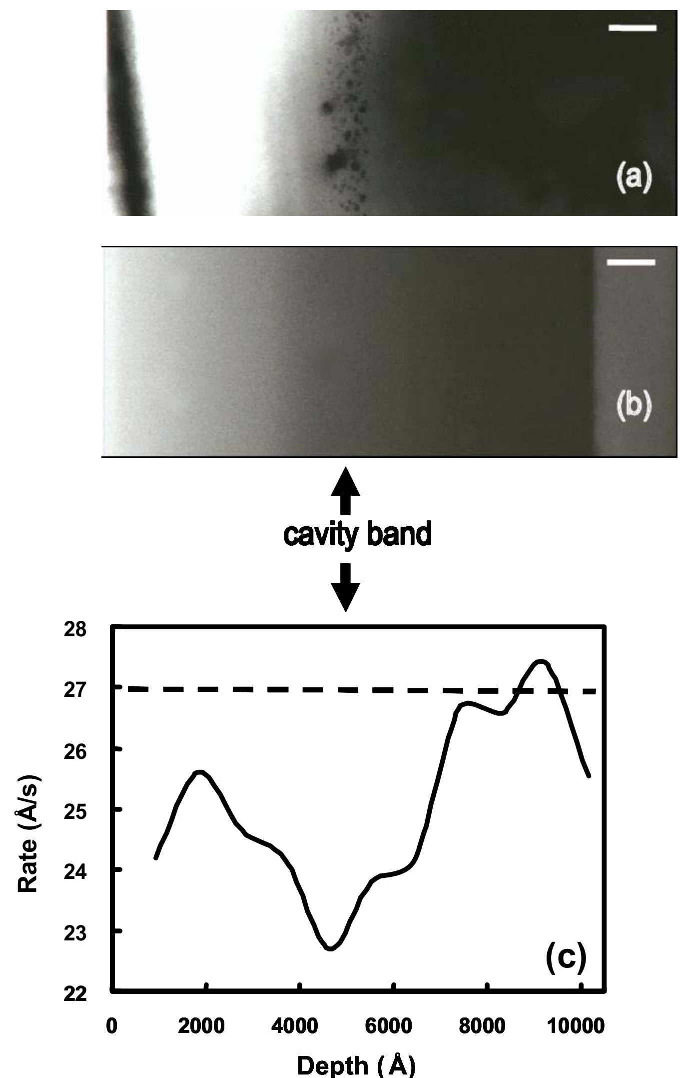

Fig. 1(a) [110] bright-field XTEM image of cavity band at 5500 Å; **(b)** XTEM micrograph of a-Si sample after amorphization of the cavity band region; **(c)** SPEG rate (at 625 ^{o}C) of a-Si layer originally containing the cavity band normalized to normal a-Si with H effect (the dash line shows the intrinsic SPEG rate). Scale bar is 100 nm.

smaller open volume defect, making the preferential amorphized Si less dense than a typical a-Si (or structurally intrinsic a-Si as discussed before). It is expected that the presence of such small open volume defects in amorphous structure would not be easy to detect in a standard TEM image. We also met difficulty in detecting the existence of such a less dense a-Si by electron energy loss spectroscopy (EELS) and radial distribution function (RDF) analysis. The highly localized, less dense amorphous structure in the region where the original cavities have collapsed by shrinkage did not giving the enough information for the statistic analysis. However, the negative result of the above experiments does not rule out the supposed presence of the less dense amorphous structure.

Fig.1(c) shows the rate of SPEG of the as-implanted a-Si layer as shown in Fig. 1(b). Fig.2 shows the corresponding activation energy E and preexponential factor V_0 of SPEG of the a-Si layer at three temperatures: 530, 600 and 670°C. All these data were extracted from measured TRR data via fitting to its corresponding theoretical function of reflectivity versus c/a interface position using a novel computer program we developed on the base of the procedure as described in [9]. In doing so, the relative error for the rate is within 5% (The details about the fitting program [17] will be published somewhere else). Clearly, both an increased activation energy and an increased preexponential factor of SPEG are obtained, indicating a slow down in regrowth rate in the region originally containing the cavities compared with normal self-ion implant-induced a-Si (or structurally intrinsic a-Si). However, the retardation of SPEG does not prevent complete regrowth to the surface and, when the regrowth front completely passes through the original cavity band region, the regrowth kinetics return to normal. As analyzed previously, the original open volume of the cavities should be conserved even if the cavities totally collapse. Thus, the open volume in cavities could have been dissociated and then redistributed quite locally within a-Si during irradiation, leading to a less dense a-Si in the original cavity band region. This less dense a-Si cannot prevent SPEG but could be responsible for the retarded rate, the increased E_a

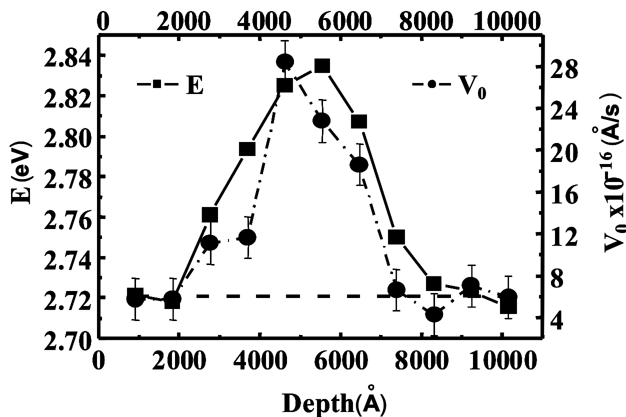

Fig.2 Activation energy E (eV) and preexponential factor V_0 (Å /s) of SPEG rate vs depth (Å) for the amorphised Si layer as shown in Fig.1(b) originally with the nanocavity band as shown in Fig.1(c). The dashed line is approximate value of the "normal" activation energy (~2.70 eV) and preexponential factor (~ $5x10^{-8}$ cm/s).

and the increased V_o in the SPEG. It is probable that an excess of dangling bonds in the locally less dense a-Si in the region originally with the cavity band could be responsible for this SPEG behavior. In terms of computer modeling, the dangling bonds in a-Si are believed to be configured by removal of about three atoms or so [18] from the centre of a continuous random network. These excess dangling bonds in the original cavity band region are very stable and should not disappear under structure relaxation but contribute to the enhancement both in the activation energy and in the attempt frequency during SPEG. The retardation of SPEG, in the presence of such dangling bond clusters, may be a result of the extra number of Si atoms required for elimination of dangling bonds by special structural arrangements in the less dense a-Si layer [19]. In detail, the less compressive or tensile stress field within the less dense a-Si could contribute to the retardation in SPEG rate and the corresponding increase in activation energy because of a negative activation volume [20] in SPEG of a-Si. As pressure P decreases, an increase in activation energy E can be predicted from the relation:

$$(\partial E/\partial P)_T = -\Delta V^*, \quad (1)$$

where $-\Delta V^*$ is the negative activation volume. The increase in the preexponential factor, which is related to the attempt frequency of atoms in the c/a interface during SPEG can be attributable to the deficiency of atoms in the less dense a-Si region with dangling bonds. This is because, in a dangling bond, its mass m is smaller compared with a normal bond. Therefore, an increase in attempt frequency or V_o can be predicted as well from relations:

$$f \propto (k/m)^{1/2}, \quad (2)$$

and

$$V_o \propto f\lambda, \quad (3)$$

where k and λ is elastic constant and step distance of atom jump.

Although the dangling bonds in the less dense a-Si should be source for the SPEG behaviour, the residual hydrogen in the cavity band region is an inevitable accompanying factor to be clarified in elucidation of the mechanism of SPEG retardation. Full details of treatment of the TRR data and SPEG kinetics [17] are not given here but we note here that both a-Si layers (initially with and without cavities) exhibited the expected ~ 20% slowdown in regrowth in the top 1/2 μm or so as a result of indiffusion of hydrogen [2]. However, before annealing the sample originally containing cavities showed an additional H concentration peak at the cavity depth, but this H peak disappeared after SPEG as detected by a very sensitive SIMS [21]. Obviously, the addition al H peak is remnant from the original cavity band and could become trapped at the additional dangling bonds formed from the collapse of the cavities via amorphization (such H passivation would help to stabilize the additional dangling bonds). This residual H along with the passivated Si vacancies could be

segregated at the moving c/a interface during SPEG and be removed to the surface. Further analysis [20] shows that the remnant H before SPEG annealing does not extend over all the amorphous region where there is retardation of rate and corresponding increase in activation energy and preexponential factor. This may suggest that H along with the vacancies redistributed during annealing and influence the kinetics [2] during SPEG. Alternatively, the main reason for the changes in SPEG kinetics may not be related specifically to residual H but directly to the structural changes (residual open volume "defects") in a-Si at the depth of the original cavity band. Such open defects are strong sinks for trapping H which indiffuses into a-Si during annealing. Thus, the observed increase of E in the amorphous region where H concentration is obviously higher as reported previously [2] may be not due to the existence of H as claimed but due to an existence of the excess dangling bonds. Also, from relations (2) and (3), if there is only H effect without the less dense a-Si, a V_0 lower than that of the normal a-Si should be expected at the depth of the cavity band in Fig. 2 (a) due to additional mass of the trapped H atoms. However, our data give a higher Vo than normal a-Si, suggesting that the excess vacancies are a cause of the changes in SPEG kinetics.

The above SPEG results indicate that there is a less dense a-Si structure resulting from the collapsed cavities, which can be responsible for the SPEG kinetics. However, this less dense a-Si structure can be recrystallized to essentially perfect c-Si. Another supportive experimental fact is that such a modified a-Si structure behaves surprisingly the same in affecting the kinetics of SPEG as the modified a-Si structure by excess vacancy region induced via high dose self-implanted a-Si, as discussed [17]. Both modified a-Si structures, although induced via two different non equilibrium processes of implantation, show all in the same way a retarded rate, an increased E, and an increased V_0 during SPEG, if compared with normal a-Si. This implies that both would have the same less dense structure. In both cases additional H appears only to be trapped on an excess dangling bonds associated with less dense a-Si. In other words, there would be no excess H trapped if there are no excess dangling bonds in the first place associated with less dense a-Si.

We also examined the microstructure and attempts at Au gettering in a sample where the cavity band region was amorphised and subsequently recrystallised using XTEM and RBS-C analysis [17] (data not shown here). The XTEM result clearly illustrates the complete disappearance of the cavity band in this case. Indeed, the Si region originally containing cavities is now essentially defect-free and therefore H-free: the only disorder is in the Si near-surface (Au implant damage) and at the original a-Si / c-Si interface where H may be still trapped. The latter interface disorder consists of well-defined dislocation loops, which result upon annealing at 850 ^{o}C. The RBS Au profile after 850 ^{o}C annealing shows a lack of gettering of Au to the original cavity band region, suggesting the absence of any appreciable open volume defects [10] or disorder to getter Au at the original depth of the cavity band.

ACKNOWLEDGMENT

The author would like to express sincere appreciation for the critical discussions and full support from Professor Jim Williams in the Department of Electronic Materials Engineering at the Australian National University. Critical discussions, continuous support and encouragement from Professor Z. G. Wang in the Key Lab. of Semiconductor Materials Science, the Chinese Academy of Sciences, Professors R. Averback, K. C. Hsieh, K. Kim, and Ian Robertson in the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign are specially acknowledged.

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