

Diffusion and reaction kinetics governing surface blistering in radio frequency sputtered hydrogenated a-Si_xGe_{1-x} (0 ≤ x ≤ 1) thin films

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Keywords: amorphous silicon germanium; hydrogen; annealing; blisters; sputtering

Abstract

The preparation of blister free layers of hydrogenated a-Si_xGe_{1-x} (0 ≤ x ≤ 1) is a primary requisite for their technological applications. In RF (Radio Frequency) sputtered layers the formation of blisters is temperature dependent, as also shown here. This dependence is used to propose a theoretical model aimed at a better understanding of the mechanisms determining the blistering. Beside the reaction kinetics responsible for the release of H atoms from SiH and/or GeH complexes the model takes into particular account the contribution of the diffusion of H. The activation energy for blistering also enters in the model. The validation of the theoretical frame of the model is confirmed by the fact that it predicts a blistering threshold temperature in reasonable agreement with the experiment. The amorphous hydrogenated thin layers were deposited on polished silicon by RF co-sputtering. They were annealed between 150 and 350 °C. The

structural changes of the surface of the SiGe films have been explored systematically by light beam reflection, scanning electron microscopy while the depth distribution of hydrogen was measured by secondary neutral mass spectrometry.

1. Introduction

The structural and surface quality of the material employed is one of the most critical issues as regards the large scale application of electronic devices based on hydrogenated amorphous silicon (a-Si:H), germanium (a-Ge:H) and a-SiGe:H. Atomic hydrogen migration occurs in the amorphous network. The high temperatures applied during growth of those materials, e. g. by chemical vapor deposition [1-3], or reached during device operation [2, 4] enhance the diffusion of H atoms, in particular of those liberated from their bonds to the host atoms as a consequence of annealing. Such enhanced diffusion favors the migration of H atoms towards nanovoids where they very likely form molecular H₂ since the reaction $2\text{MeH} \rightarrow \text{H}_2 + \text{Me-Me}$ is an exothermic one [5] (Me indicates the host atom: Si or Ge). The accumulation on the wall of voids causes the evolution of hydrogen bubbles and then the formation of blisters. Some efforts have been made to understand the microscopic mechanisms determining the rupture of the MeH bonds and formation of H₂ rich voids at the origin of the blisters [6-8] in order to get rid of them. For this purpose a method was recently proposed for a-Si:H which is based on the optimization of the shape, size and thickness of the layer [9]. As said above a key parameter is temperature. The objective of this paper is to find a way to determine the threshold temperature below which surface blistering does not occur in hydrogenated a-Si_xGe_{1-x}, $0 \leq x \leq 1$. This is achieved by a theoretical model that takes into account both the kinetics of the rupture of the MeH bonds and, in particular, the diffusion of the atomic H. The hydrogenated a-Si_xGe_{1-x} has been deposited by RF (Radio Frequency) sputtering. The experimental results suggesting our theoretical approach

have been obtained by SNMS (Secondary Neutral Mass Spectrometry), as regards the depth distribution of H, and by surface light reflectivity measurements, as regards the assessment, as a function of temperature, of the time of the onset of blistering and its activation energy by Arrhenius plots. The data supplied by the latter plots allow the validation of the theoretical model. The calculated critical temperature for blistering, in fact, is on the same order of magnitude as the experimentally observed one. Also, the experimentally determined Vegard's law-like dependence of the blistering activation energy on the composition x in the $a\text{-Si}_x\text{Ge}_{1-x}$ alloys is interpreted by a simple formula and related 3D-like diagram.

2. Experimental

Hydrogenated $a\text{-Si}$, $a\text{-Ge}$ and $a\text{-Si}_x\text{Ge}_{1-x}$ layers were deposited by RF sputtering in a commercial Leybold Z 400 apparatus from targets of either pure Si, pure Ge or a target assembled from different size of Si and Ge slices, respectively. The RF sputtering has been carried out under a mixture of hydrogen and argon high purity gases with an applied wall potential of 1.5 kV dc yielding a plasma pressure of 2.5 Pa. The hydrogen flow rate was kept constant at a value of 0.9% of the 2.5 Pa plasma pressure for all the deposited $a\text{-Si}_x\text{Ge}_{1-x}$ layers. The examined $\text{Si}_x\text{Ge}_{1-x}$ layers had five different compositions of $x=0.32, 0.44, 0.67, 0.74$ and 0.96 that were measured by ERDA (Elastic Recoil Detection Analysis) and by energy dispersive spectroscopy in a transmission electron microscope. All samples were 200 nm thick. The total H content was 16-18 at% in all as-grown samples as measured by ERDA. The $c\text{-Si}$ substrate was water-cooled in order to keep its temperature $\leq 60^\circ$ [10].



Fig. 1. Schematic drawing of the sample surface illumination and determination of the blistering time.

At such low temperature no blister should form during the deposition process, i.e. before the after-growth annealing experiments applied for the determination of the activation energy. This should guarantee the correct evaluation of the blistering onset. The latter event was determined by illuminating the sample with a 3 mW He-Ne laser beam with diameter of 3 mm and angle of incidence of 60° which resulted in an elliptically illuminated sample area with size of about $3 \times 6 \text{ mm}^2$. The onset time of blistering was the time elapsed between the stabilization of the temperature and the sudden start of the decrease of the reflectivity of the sample surface, caused by the outgoing rays reflected at many different angles, which was measured by a PIN detector blended with diameter of 3 mm (Fig. 1). The minimum temperature at which blisters appeared varied between 179°C for a-Ge and 271°C for a-Si. Arrhenius plots of the inverse of the minimum time needed to make the blisters optically visible vs. the inverse of the temperature were used to determine the activation energy for blistering.

The depth distribution of hydrogen in the as-prepared and annealed layers was measured by SNMS with a type INA-X instrument produced by SPECS GmbH, Berlin [11, 12]. The surface bombardment was performed at low pressure electron cyclotron wave resonance argon plasma. Direct bombardment mode was applied and the post ionized sputtered neutral particles were

analyzed by a quadruple mass spectrometer Balzers QMA 410. Ar^+ ions are extracted from low pressure plasma and bombard the negatively biased (-350 V) sample surface with a current density of $\sim 1\text{mA}/\text{cm}^2$. The investigated area was confined within a circle of 2 mm diameter by a Ta mask. To check the lateral homogeneity of ion bombardment and to determine the sputtering rate an AMBIOS XP-1 type profilometer has been used. The surface morphology of samples was analyzed by SEM (Scanning Electron Microscope) with a Hitachi S-4300 CFE machine operated in the secondary electron mode. A 15 kV accelerating voltage was used to obtain high resolution surface pictures.

3. Results

Upon annealing the layer surface changes as blisters have formed (Fig. 2a), which correspond to bubbles containing molecular H_2 [7, 13, 14]. These bubbles have developed from nano- and micron-sized cavities that have increased their volume because of the increase of the inside pressure due to the thermal expansion of the H_2 gas upon annealing [7, 13, 14]. Finally the cavities filled with H_2 pop-up and create observable blisters that transform into craters for too long annealing times or too high temperatures (Fig. 2b). Depending on temperature, the depletion of hydrogen takes place with varying amount at the beginning of the process. Number of formed blisters and craters will be lower or higher after a given annealing time, but as the SNMS results show, finally the same depth distribution of hydrogen for both Si and Ge layers is achieved (Fig. 3a).

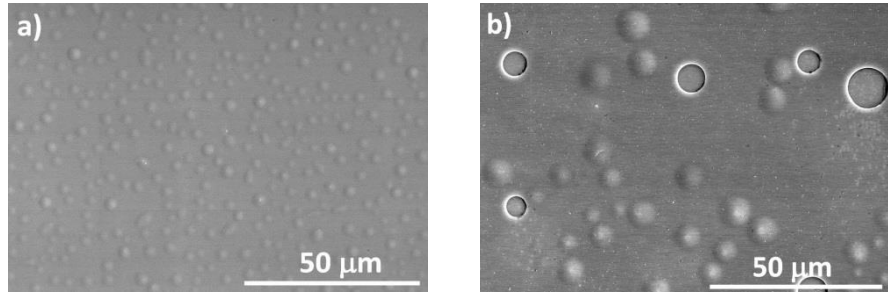


Fig. 2. SEM images of blisters and craters on annealed samples. An a-Ge:H sample has been annealed at 180 °C for 10 (a) and 40 (b) minutes.

For the a-Ge:H layers it was shown earlier by ERDA and SNMS [7] that the total H content is lower in the annealed samples with respect to the not-annealed ones. In the latter ones the amount of hydrogen decreases on going from the layer bottom, i.e. substrate side, to the top. The same measurements were repeated for a-Si:H samples, too. To have information about the time dependence of outgassing dynamics of the hydrogen in a-Si:H annealing was carried out at 180°C for a short time of 10 minutes and a longer one of 40 minutes. Figure 3b shows the depth profile before and after annealing. Significant changes in the H distribution occurs similarly to what observed in the a-Ge:H layers [7].

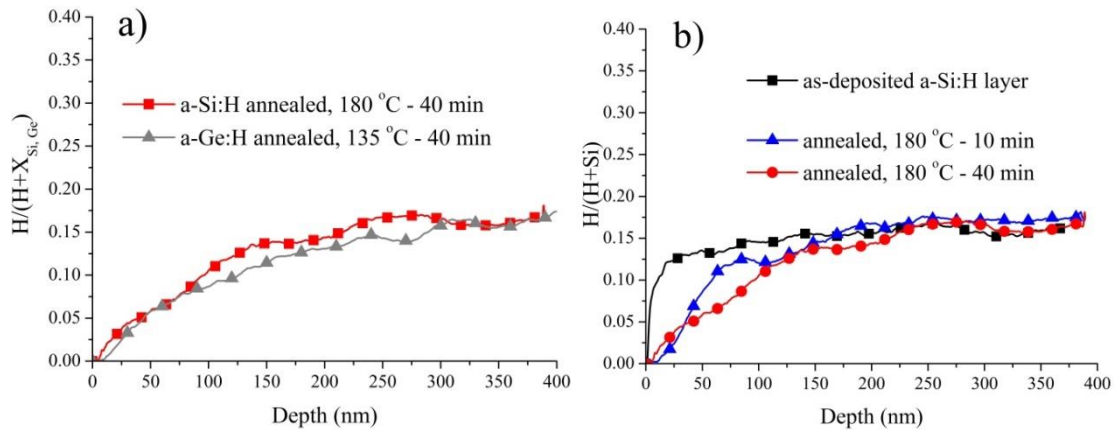


Fig.3. SNMS depth profile of hydrogen in annealed a-Si and a-Ge layer after 40 minutes of annealing (a), and after 10 and 40 minutes in a-Si layer (b).

As a result of the heat treatment, the H has left the sample and the depth distribution shows that this happened preferentially from the upper part of the layer than in the lower part. The total content of hydrogen finally gets lower in the annealed samples with respect to the not-annealed ones. The results show that the loss of hydrogen in a-Ge:H occurs faster compared to the a-Si:H layers, which may be consistent with the fact that the binding energy of GeH is lower than that of SiH [15]. Hence the liberation of H in Ge takes place earlier, i.e. at a lower temperature. However, independently of the applied higher annealing temperature after 40 minutes of annealing the distribution of hydrogen content reached the same profile as in germanium (Fig. 3a). This can suggest that hydrogen leaves the samples mostly at the beginning of the annealing process and later the same distribution is reached in both cases.

Fig. 4 shows the rate coefficient $k_{exp} = 1/t$ for the appearance of blisters on the sample surface as a function of $1000/T$ for a-Si, a-Ge and all the a-Si_xGe_{1-x} layers, except that with x=0.96, with t and T the time and temperature of the blistering onset, respectively. The plots exhibit the typical Arrhenius behavior described by the formula $k_{exp} = 1/t = k_0 \exp(-E_a/k_B T)$ where E_a is the activation energy for the formation of blisters, k_0 a pre-exponential factor, k_B the Boltzmann constant. E_a is assumed temperature independent. The activation energy in a-Si_xGe_{1-x} increases from that of pure a-Ge, $E_a^{Ge} = 1.68$ eV, to that for pure a-Si, $E_a^{Si} = 2.42$ eV, in a linear fashion as a function of the composition x as:

$$E_a(Si_xGe_{1-x}) = 0.733 \cdot x + 1.663 \text{ in eV, } 0 \leq x \leq 1.$$

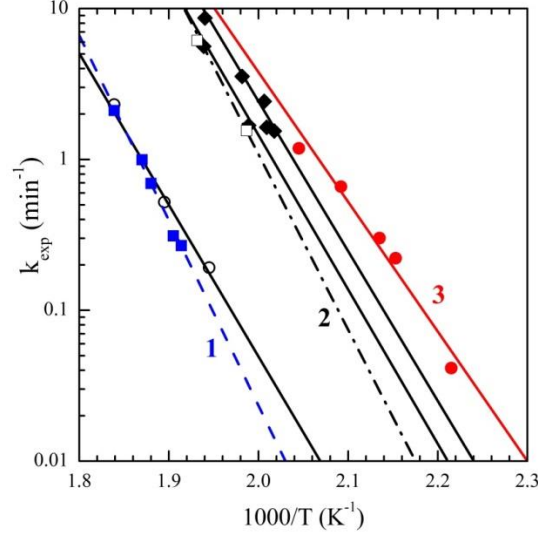


Fig.4. Arrhenius plots of $k_{\text{exp}}=1/t$ (min^{-1}) as a function of the inverse temperature for six samples. For the sake of clarity the correspondence between composition and curve is indicated for only three samples as follows Si (blue dashed curve 1) with $E_a = 2.42$ eV, $\text{Si}_{0.74}\text{Ge}_{0.26}$ (black dot-dashed curve 2) with $E_a = 2.25$ eV and Ge (red solid curve 3) with $E_a = 1.68$ eV.

It can thus be concluded that the activation energy for blistering investigated in a relatively narrow temperature range in hydrogenated a- $\text{Si}_x\text{Ge}_{1-x}$, $0 \leq x \leq 1$, varies as a function of the x composition according to the law

$$E_a(\text{Si}_x\text{Ge}_{1-x}) = x \cdot E_a^{\text{Si}} + (1-x) \cdot E_a^{\text{Ge}} \quad (1)$$

which shows that $E_a(\text{Si}_x\text{Ge}_{1-x})$ is related to the activation energies in pure Ge and Si in a fashion characteristic of the Vegard's law which is typically valid, e.g., for the lattice parameter [16] as well as the energy band gap [17] in compound semiconductors.

By applying the general law $k_{\text{exp}} = k_0 \exp(-E_a/k_B T)$ to eq. (1) the latter one can be transformed to

$$k_{\text{exp}} \propto k_{\text{Si}}^x \cdot k_{\text{Ge}}^{(1-x)} \quad (2)$$

the logarithm of which can be graphically represented by a polar coordinate system (Fig. 5). The measured values of k_{exp} are located on the x section of the cone, i.e. $x=1$ belongs to the Si and the $x=0$ to the Ge Arrhenius plot.

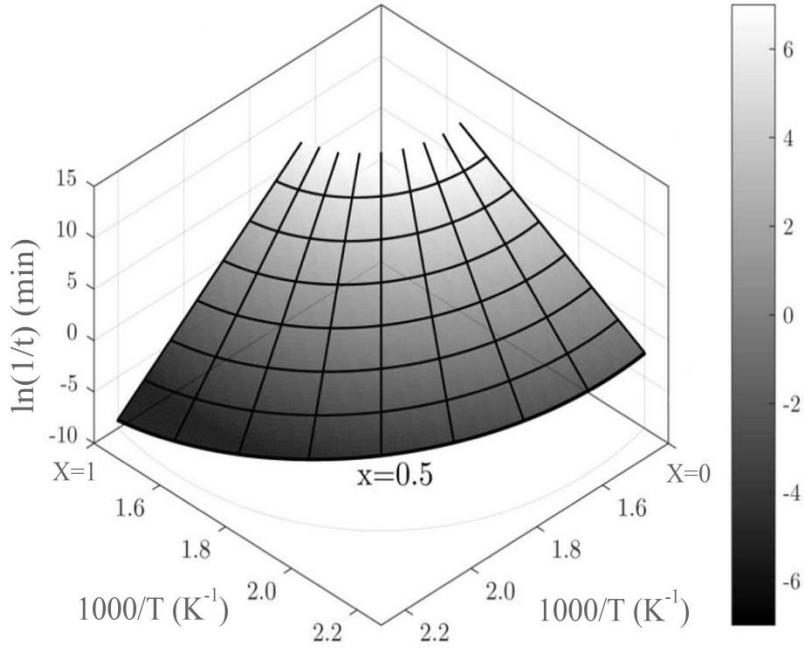


Fig. 5. Graphical representation of eq. (2) in a polar coordinate system. The left-hand vertical plane belongs to the Si and the right one to the Ge Arrhenius plot.

4. Discussion

It has been widely demonstrated that in amorphous Ge, Si and SiGe [7, 8, 15, 18], as well as in other materials [19], the reason for the formation of blisters is the increase of the volume of voids containing molecular H_2 until they pop up and deform the surface. In as-grown hydrogenated $a-Si_xGe_{1-x}$, $0 \leq x \leq 1$, H is mostly bound to the host atoms Si and Ge. Such bonds are broken when energy is supplied during an annealing according to the following reactions [15]



and the liberated H can form H_2 by



Our earlier work [15] revealed that the rate coefficient of anyone of the reactions (3) and (4) is

$$k = k_0 \cdot \exp\left(-\frac{E^m}{k_B T}\right) \quad (6)$$

where E^m is the binding energy of H to the metal atom, either Si or Ge. By considering that in $\text{Si}_x\text{Ge}_{1-x}$ H is bound to Si and Ge in proportion to their concentrations and evaluating the variation in time of the SiH, GeH and H_2 concentrations it was shown also theoretically elsewhere [15] that the activation energy of blistering $E_a(\text{Si}_x\text{Ge}_{1-x})$ in a- $\text{Si}_x\text{Ge}_{1-x}$ is related to those in a-Si and a-Ge by a Vegard's-law-like expression just the same as the experimental one of eq. (1).

Comparison between the SNMS results and the series of annealing experiments suggests that there must be a temperature below which the blistering process cannot be observed and whose existence is determined by a diffusion process considered to be general. Fick's first law relates the diffusion flux to the concentration under the assumption of steady state. It postulates that the flux of atomic H goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient. In one dimension perpendicular to the surface of the substrate, the law is:

$$\frac{n_H(T)}{At} = -D(T) \frac{dc_H(x)}{dx} \quad (7)$$

where, $n_H(T)/At$ – the "diffusion flux" – is the number of atomic H per unit area and time (dimension $\text{cm}^{-2}\cdot\text{sec}^{-1}$), $D(T)$ the diffusion coefficient and $c_H(x)$ the concentration of atomic H (cm^{-3}) and t denotes the time at which the $n_H(T)$ – number of the atomic H – is generated. For a quick approximation of the H concentration the SNMS results (Fig. 3) can be used:

$$\begin{aligned} c_H(x) &= c_H && \text{if } 0 < x < \delta, \text{ and} \\ c_H(x) &= c_H \cdot \left(1 - \frac{x}{d}\right) && \text{if } \delta < x < d \text{ and } \delta < d \end{aligned}$$

where d is the thickness of the whole deposited layer. Here we suppose that the concentration decays from the substrate surface where the concentration of H is equal to the c_H original value. The approximation was suggested by the SNMS plots demonstrating the H concentration after relatively long annealing times at temperature below 200°C. This concentration profile was developed by the long term steady state during the outdiffusion process caused by low temperature annealing. It seems appropriate to record this moment in the diffusion equation to determine the critical value of the temperature T^* where still no blistering occurs; the chosen concentration profile establishes the equilibrium state when the gradient of diffusion is small ($x = d$) and the highest c_H value of the concentration is located at the surface of the substrate where the highest probability of the blistering onset can be expected. We note that the diffusion in one dimension from a boundary located at position $x=0$ would be exactly expressed by the complementary error function *erfc* [20, 21] but all of our assumptions is only intended to be limited at testing of an equilibrium model where atomic H formation and its diffusion are balanced. By entering these definitions into Eq. (7), one gets

$$\frac{n_H(T)}{At} = D(T) \frac{c_H}{d} \quad (8)$$

To estimate the number of the H atoms $n_H(T)$ we apply our earlier results from [13] where thin Si and Ge layers were annealed at relatively high temperature ($\theta=350^\circ\text{C}$) to determine the amount of H that has left the sample. Let choose these layers with thickness $\delta=40\text{nm}$ to be located at the interface of the layer to the substrate. This layer provides atomic H for the second part of the film (mentioned in section Experimental) of thickness $d = 200\text{nm}$ being annealed at temperature T^* . From ERDA measurements the Si:H or Ge:H (commonly Me:H) layers had an as-deposited H concentration c_H of 16 and 6 at%, respectively. Let express the liberated amount of the atomic H by a percentage r^m of the original concentration: $r^m \cdot c_H$. The ERDA measurements demonstrated

that, after the annealing at $\theta=350^\circ\text{C}$, 11 and 4 at% H has left the layer Si and Ge, respectively. Hence $r^{Si}=0.11$ for Si and $r^{Ge}=0.04$ for Ge. The H would leave the layer with thickness $\delta=40\text{nm}$ located at the interface to the substrate in H_2 molecular form because blistering would be followed by crater formation [7]. However, since in our case the critical temperature T^* we are looking for is by *definition* lower than the temperature θ there is no interface at the $x=\delta$ line in our model; no bubble is formed and thus no H_2 is produced. The liberated $n_H(T)$ atomic H diffuses from the layer forming a flux perpendicular to the surface of the layer. If N_H is the number of the total Me-H bonds in the volume considered in the sample before the annealing procedure at temperature θ , i.e. $N_H = c_H \cdot A\delta$, then the following rate coefficient of each one of the reactions can be used:

$$\frac{n_H(T)}{N_H} = k_0 \cdot \exp\left(-\frac{E^m}{k_B T}\right) \quad (9)$$

$$\frac{n_H(\theta)}{N_H} = r^m = k_0 \cdot \exp\left(-\frac{E^m}{k_B \theta}\right) \quad (10)$$

after dividing these two equations we get

$$n_H(T) = r^m \cdot c_H \cdot A\delta \cdot k_0 \cdot \exp\left(-\frac{E^m}{k_B T}\right) \quad (11)$$

where $k_0 = \exp(E^m/k_B\theta)$ and $T < \theta$.

The series of measurements performed at θ is not appropriate to establish the time t at which the $n_H(T)$ is generated since it would be extremely short to observe it. The time t will be estimated with simple tools: blisters appear abruptly on the surface in the case of Me layers during the annealing. Based on this, we assume that blistering occurs at the time t_{bl} when the number of the accumulated H_2 molecules reaches the critical N_{bl} number and the critical pressure as a consequence of the general gas law. The accumulation process in time can be described by $k_{exp} \cdot t = N_H/N_{bl}$ where k_{exp} is the rate coefficient of reaction and N_H the number of accumulated

H₂ molecules. Inserting the time of appearance of blisters observed in the experiments we get a simple relation enabling the Arrhenius plot (Fig.4) to explore atomic scale processes

$$k_{exp} \cdot t = 1 \quad \text{or} \quad \frac{1}{t} = k_{exp} = k_0^a \cdot \exp\left(\frac{-E_a^m}{k_B T}\right) \quad (12)$$

and this time will be used as generation time. Inserting Eqs. (11) and (12) into Eq. (8) the following eq. (13) is obtained relating the number of H atoms produced by the rupture of the Me-H bonds and those moving by diffusion

$$k_0^a \cdot \exp\left(\frac{-E_a^m}{k_B T}\right) \cdot r^m \cdot c_H \cdot \delta \cdot k_0 \cdot \exp\left(-\frac{E^m}{k_B T}\right) = D(T) \frac{c_H}{d} \quad (13)$$

Let express $D(T)$ in the usual way:

$$D(T) = D^m \cdot \exp\left(-\frac{E_d^m}{k_B T}\right) \quad (14)$$

with E_d^m the energy barrier for diffusion of Me, i.e. either Si or Ge, and D^m the related pre-exponential factor. It has to be noted that eq. (13) does not depend on $A \cdot c_H$ any more, i.e. on the H concentration of the as deposited case.

$$r^m \cdot d k_0^a \cdot \exp\left(-\frac{E_a^m}{k_B T}\right) \cdot \delta k_0 \cdot \exp\left(-\frac{E^m}{k_B T}\right) = D^m \cdot \exp\left(-\frac{E_d^m}{k_B T}\right) \quad (15)$$

To determine the critical value of the temperature T^* , where still no blistering occurs, one has to solve this equation for T . This is obtained by imposing the equilibrium between the number of the liberated H and the number of H able to move by diffusion. The number of the liberated H is weighted by the exponential function of the temperature (Eq. 11) and increases rapidly with increasing temperature resulting in the accumulation of H₂ molecules in the voids.

By using $E_a^m = 2E^m - E_{H_2}$ [15] one arrives at

$$\ln k_0 + \ln \left(r^m \frac{\delta \cdot d \cdot k_0^a}{D^m} \right) = \frac{3E^m - (E_{H_2} + E_d^m)}{k_B T^*} \quad (16)$$

E_{H_2} is the bond energy of the H_2 molecule (4.50 eV) [22,23]. It is recalled here that k_0^a are the pre-exponential factor of the rate coefficient of the reaction governing the onset of blistering (see eq. (12)), $\ln k_0 = E^m/k_B\theta$ and E^m are defined in eq. (6) and $\theta = 623^\circ\text{K}$.

Eq. (16) allows the evaluation of T^* by using the following parameters common to all samples: $\delta d = 8 \times 10^{-11} \text{ cm}^2$ for a layer thickness of 200 nm, $k_B = 8.6 \times 10^{-5} \text{ eV/K}$, $E_{H_2} = 4.50 \text{ eV}$. Note that r^m , δ and k_0^a as well as d and k_0^a are related each other; using this T^* concept for a given deposition technology it is necessary to check this value by a series of Arrhenius plots. In the case of $\text{Si}_x\text{Ge}_{1-x}$ films the Eq. 1 and 2 can be automatically used and we cannot go wrong by using

$$r^m = x \cdot r^{Si} + (1 - x) \cdot r^{Ge}$$

a Vegard's law like formula. $r^{Si}/r^{Ge} \approx 3$, is an agreement with Sayama's preferential attachment ratio [24].

In the case of Si $\ln k_0^a = 48.853$ from Fig. 4 converted into sec^{-1} , $r^{Si} = 0.11$ as reported above, while $E^m = 3.45 \text{ eV}$ [15]. By using Branz's results about the diffusion coefficient of H in a-Si [25], i.e. $E_d^m = 1.85 \text{ eV}$ and $D_m = 10^{-4} \text{ cm}^2/\text{sec}$, T^* turns out to be 473°K (200°C).

For Ge $\ln k_0^a = 36.148$ from Fig.4, $E^m = 3.10 \text{ eV}$ [15], while $E_d^m = 1.7 \text{ eV}$ and $D_m = 4 \cdot 10^{-9} \text{ cm}^2/\text{sec}$ according to [26] giving $T^* = 402^\circ\text{K}$ (130°C). These are the results for the critical temperature below which the blistering process cannot be observed. They are in reasonable agreement with experiment since the minimum experimental temperature for blistering was 271 and 179°C for Si and Ge, respectively and confirm that eq. (16) can be useful to have a quite reliable estimation of the temperatures that should not be overcome in hydrogenated a- $\text{Si}_x\text{Ge}_{1-x}$

($0 \leq x \leq 1$) in order to prevent surface blistering. Eq. (13) indirectly includes the technological parameters (e.g. density of voids) of the layer being studied, as the thin source layer characterized by k_0^a and r was made with a similar sputtering technology.

It is worth noticing that the critical temperature for blistering T^* weakly depends on the thickness d as actually observed experimentally. Comparing to the eq. (16), we get that T^* decreases about 3°C when a sample with a thickness of 400nm (i.e. twice as thick as the sample) were annealed. Moreover, the results also agree with Branz's data [25] for the diffusion coefficient of Si (a p-type target was used for SiGe). At present no explanation is available for the little strange value of $E_d^m = 1.7\text{eV}$ for Ge.

Conclusion

This work reviewed the SNMS results and the series of annealing experiments of the RF sputtered hydrogenated amorphous silicon (a-Si:H), germanium (a-Ge:H) and a-SiGe:H layers. The comparison suggests that there must be a temperature below which the blistering process cannot be observed and whose existence is determined by a simple diffusion process. A model was drawn up for estimation of the critical temperature empirically. The thin part of the layer located at the interface to the substrate provides atomic H for the other part of the deposited film above it. The atomic H liberated in the interface section drifts across a part where the concentration gradient is supposed to be linear. Relation was obtained by imposing the equilibrium between the number of the liberated H atoms and the number of those able to move by diffusion. Investigating a deposited SiGe layer by a series of Arrhenius experiments the critical temperature can be estimated and the diffusions parameters discovered if the critical temperature is known. The temperature range at which blistering onset was detected concerns

temperatures often applied for the a-Si_xGe_{1-x} growth, e.g. by chemical vapour deposition, or during device manufacturing processes and close to the operating temperature of solar cells; therefore the findings reported here can be important regarding the quality and lifetime of photovoltaic, microelectromechanical systems, bolometer and black matrix materials and devices.

Acknowledgements

Work supported by the Scientific Cooperation Agreement between MTA (Hungary) and CNR (Italy). The SNMS measurements were carried out in the frame of the GINOP-2.3.2-15-2016-00041 project, which is co-financed by the European Union and the European Regional Development Fund.

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