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Decay-kinetics study of atomic hydrogen in *a*-Si:(H,O,N) and natural beryl

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A method of data processing was applied to study the decay kinetics of interstitial atomic hydrogen in x-irradiated *a*-Si:(H,O,N) and uv-irradiated natural beryl. It was assumed that the interstitial atomic hydrogen was produced by radiolytic irradiation of *R*-H type molecules and trapped at interstitial sites of both materials. The heating releases the atomic hydrogen which quickly is either retrapped, recombined with *R* radical left in the matrix, or combined with other atomic hydrogen atoms forming H_2 molecules. The parameters related to untrapping and recombination processes were found to obey the Arrhenius law. On the other hand, the retrapping and H_2-formation parameters were also fit to a function proportional to $(T^{1/2}-T_0^{1/2})$, where T_0 is a constant.

I. INTRODUCTION

Atomic hydrogen has been studied in several crystalline and amorphous matrices for about four decades. Unfortunately, there are still very few systematic studies of the hydrogen centers concerning thermal decay kinetics. Recent studies in *a*-Si:(H,O,N),[1] natural beryl,[2] barium aluminoborate glasses,[3,4] and tourmaline[5] report interesting results from atomic hydrogen thermal decay electron-paramagnetic-resonance (EPR) measurements.

The H_i^0 observed in barium aluminoborate glasses is unstable at room temperature.[3] The kinetics of this center was analyzed in terms of the Levy's model[6] yielding three first-order processes, each one having a different activation energy. In contrast, the measured thermal decay of the H_i^0 in find tourmaline,[5] stable at room temperature, follows first-order kinetics.

Pontuschka *et al.*[1] observed that the x-irradiated hydrogenated amorphous silicon containing oxygen and nitrogen impurities *a*-Si:(H,O,N) shows the characteristic H_i^0 doublet in the EPR spectrum. The absence of this center in x-irradiated nominally pure *a*-Si:H led to the conclusion that the presence of oxygen is needed to stabilize this center. Second-order thermal decay kinetics was assumed in the analysis of the data yielding an activation energy of about 0.5 eV. Samples were irradiated at room temperature until saturation. A series of EPR measurements was performed to study the isothermal decay of the atomic hydrogen centers. The measurements were carried out at 310, 319, 323, 332, and 343 K, respectively.

Atomic hydrogen, stable at room temperature, was observed in x-irradiated beryl by Koryagin and Grechushnikov[7] in 1966 and by Bershov[8] in 1970. When beryl was completely dehydrated, H_i^0 was not detected, leading to the conclusion that it originated from the H_2O radiolysis.[7] Blak *et al.*[9] also observed EPR of H_i^0 centers in beryl, uv irradiated at room temperature. Isothermal decay measurements at 353, 373, 393, 413, 433, and 453 K could not be described in terms of first- or second-order kinetics.[2] This result suggests the superposition of several kinetic processes occurring together. It is not difficult to write down the differential equation for each possible reaction.

Recent ionic thermocurrent (ITC) measurements in beryl[10] showed that heat treatments between 1000 and 1200 K produce the disaggregation of clusters of water molecules and bond breaking into OH^- and H^0. Above 1200 K a subsequent water disappearance was observed. When the samples, thermally treated between 1000 and 1200 K in order to produce clusters disaggregation, were uv irradiated, the intensity of the ITC OH^- bands increased. It was concluded therefore that the efficiency of the water photodissociation under uv irradiation was considerably improved. For lower tempertures an aging process was observed and the decrease of the intensity of the OH^- bands was attributed to a reaction of the type $OH^- + H^0 \rightarrow H_2O^-$.

Exact solutions of systems of chemical kinetics differential equations can easily become laborious or even prohibitive in most cases. For this reason one resorts to numerical integration, which, with the present-day easy access to personal computers, is quite manageable.

II. KINETIC EQUATIONS

We assume that the atomic hydrogen is produced during uv and x irradiation of beryl and *a*-Si:(H,O,N) samples by photodissociation of *R*-H-type molecules leaving H^0 and *R* radicals. In beryl, *R* is assumed to be OH^-, which results from the dissociation of H_2O. In *a*-Si:(H,O,N), *R* is part of the disordered chain of its amorphous structure that lost an atom of hydrogen during irradiation, leaving a dangling bond. The H^0 diffuses throughout the interstices of the network before being recombined or trapped in stabilizing sites, where the presence of oxygen is essential. Such a site should be a potential well of depth E_α (see Fig. 1) where the nature of the repulsive forces performed by the walls are due to Pauli exclusion repulsive interaction with neighboring filled oxygen external orbitals. This obviously requires a

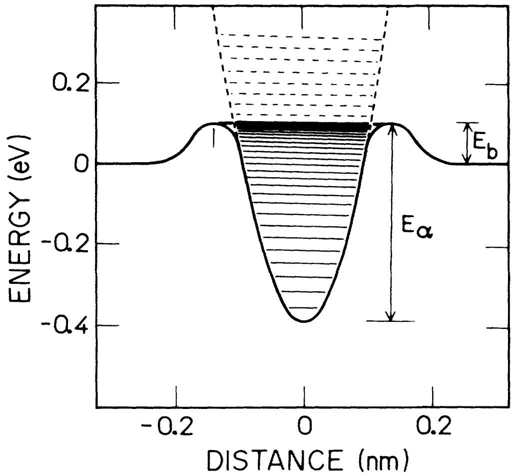

FIG. 1. Sketch of the potential energy of H^0 trapped in the oxygen neighborhood stabilizing site.

minimum number of neighboring oxygen atoms, sufficient to form a cage. Inside this limited volume, the neutral atomic hydrogen is nearly free, its paramagnetic nature being preserved. After a sufficient time of irradiation, all the available H^0 traps are filled and the growth of the concentration of interstitial atomic hydrogen $[H_i^0]$ (the brackets are referred to as concentration) reaches saturation. In the following the subsequent notation will be adopted: *R*, recombination center; H, trapping site; H_t, trapped H_i^0; H_f, free H_i^0 diffusing throughout the sample; *R*H, molecules or macromolecules; *S*, empty traps.

On heating, H_t overcomes the trapping potential energy depth E_α and moves throughout the lattice[11] prior to the reactions of retrapping, recombination with dangling bonds, or combination between a pair of H_f forming a H_2 molecule. There is a very simple reason to rule out the bond-breaking diffusion[12-16] or mediated by the dangling and/or floating-bond migration model[17,18] as the mechanism of the thermal annealing of $[H_i^0]$, as observed by EPR: After the untrapping from its stabilizing site, the neutral atomic hydrogen is no more observed after the first covalent bonding could take place, either by recombing with a dangling bond or by breaking a weak Si—Si bond.[19] This situation is irrevesible, even if the motion of the bonded hydrogen proceeds further by means of a hopping mechanism. The paramagnetic neutral hydrogen was only observed after the sample irradiation. Therefore, the atomic hydrogen untrapping activation energy is related to the energy depth E_α of its particular trapping site and should not be confused with the activation energy of bonded hydrogen diffusion, which is equal to 1.53 eV.[12]

Assuming that the total number of H_i trapping sites is constant, i.e,

$$[H_t]+[S]=[N] , \tag{1}$$

where $[N]$ is the concentration of trapping sites, the change rates of $[H_t]$, $[H_f]$, $[S]$, $[R]$, $[RH]$, and $[H_2]$ are described by the following differential equations:

$$\frac{d}{dt}[H_t]=-\alpha[H_t]+\gamma[H_f](N-[H_t]) , \tag{2a}$$

$$\frac{d}{dt}[H_f=\alpha[H_t]-\gamma[H_f](N-[H_t])$$
$$-\beta[H_f][R]-\delta[H_f]^2 , \tag{2b}$$

$$\frac{d}{dt}[R]=-\beta[H_f][R] , \tag{2c}$$

where α, β, γ, and δ are adjustable parameters.

The above equations were normalized assuming that all sites are filled. The initial conditions are given by $N=1$, $[H_t](0)=1$, $[H_f](0)=0$, and $[R](0)=1$. The coupled differential equations (2) were solved using the numerical method of Runge and Kutta.[20-22] The coupled differential equations (2) were numerically solved with parameters fitted by a trial and error method, after few iterations.

III. RESULTS

The experimental values used in this work were taken from Refs. 1 and 2 for applying the numerical method described in Sec. II.

The diffusion of H_f throughout the interstices of an *a*-Si network probably roughly follows the Maxwell speed distribution for free particles. Thus the mean speed of H_f is roughly given by$v=(2kT/m_H)^{1/2}$, where m_H is the effective mass of H_f. If *d* is the collision mean free path, the frequency of collisions of H_f with Si atoms is given by v/d and the mean free time is d/v. We assume that the mean life of the excited electron spin state is longer than the mean life of collision spin-lattice relaxation. In this case, the uncertainty $\Delta\tau$ in the mean life of the electronic excited spin state is roughly the mean free time d/v. The uncertainty ΔE of the excited-spin-state energy is about $g\beta\Delta H$, where ΔH is the linewidth. Then, using the Heisenberg uncertainty principle, we obtain a EPR linewidth of about 5×10^4 G. Such a broad line is

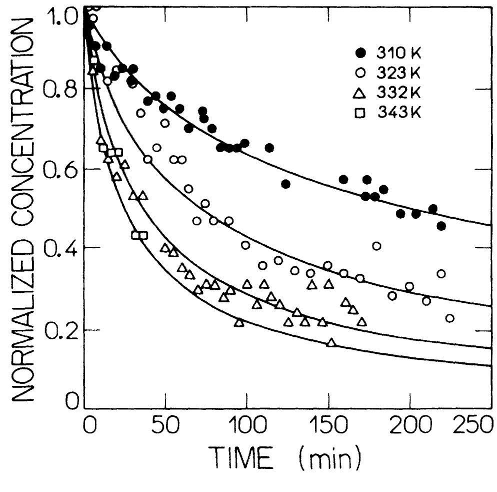

FIG. 2. Numerical integration results (solid lines) adjusted to the experimental points of the isothermal $[H_t]$ decay in *a*-Si:(H,O,N) (Ref. 1).

TABLE I. Parameters α, γ, and δ for *a*-Si:(H,O,N).

T (K)	α (s^{-1})	γ (s^{-1})	δ (s^{-1})
310	$1.25^{+0.03}_{-0.05}$	$28.5^{+3.5}_{-1.5}$	165^{+5}_{-25}
323	$2.9^{+0.2}_{-0.2}$	$37.5^{+1.5}_{-2.5}$	215^{+15}_{-10}
332	$5.1^{+0.4}_{-0.3}$	$43.5^{+2.5}_{-4/5}$	250^{+20}_{-20}
343	$7.0^{+0.5}_{-1.0}$	51^{+9}_{-11}	295^{+35}_{-65}

TABLE II. Parameters α, β, γ, and δ for beryl.

	α (s^{-1})	β (s^{-1})	γ (s^{-1})	δ (s^{-1})
353	$3.45^{+0.15}_{-0.15}$		$24.5^{+1.0}_{-1.0}$	$9.8^{+0.8}_{-0.8}$
373	$6.7^{+0.2}_{-0.2}$		$30.0^{+1.0}_{-1.0}$	$11.5^{+1.0}_{-0.7}$
393	$13.8^{+0.6}_{-0.4}$	$0.14^{+0.05}_{-0.03}$	$35.0^{+1.5}_{-0.5}$	$13.5^{+0.5}_{-1.0}$
413	$24.0^{+0.5}_{-0.5}$	$1.0^{+0.2}_{-0.1}$	$41.1^{+1.0}_{-1.0}$	$15.5^{+0.5}_{-0.9}$
433	44^{+2}_{-1}	6^{+1}_{-1}	$46.0^{+0.5}_{-1.0}$	$17.0^{+0.5}_{-0.5}$
453	72^{+2}_{-6}	20^{+1}_{-2}	$50.0^{+0.8}_{-0.8}$	$19.0^{+0.8}_{-0.6}$

undetectable by EPR, and once the motion of H_f is such that the linewidth is too large to enable H_f to be detected by EPR, the observed signal was attributed to H_t exclusively.

The numerical integration results (solid lines) adjusted to the experimental points for the isothermal decay of atomic hydrogen for x-irradiated *a*-Si:(H,O,N) is shown in Fig. 2 where β was assumed to be zero. Here the recombination centers are ignored, because the large potential barrier for the insertion of H_f in a weak Si—Si bond makes this process less probable, within the temperature range of measurements, than the process of formation of H_2. The best-fit parameters are shown in Table I. The results of our calculations are in good agreement with the assumption proposed by Pontuschka *et al.*[1] ascribing the principal process involved in the removal of hydrogen from *a*-Si:H to the formation of H_2.

The best fit (solid lines) for the $[H_t]$ decay of uv-irradiated beryl is shown in Fig. 3. The β value was no longer negligible as occurred for *a*-Si:(H,O,N). The calculated parameters are listed in Table II.

The Arrhenius law applied to the α parameter of *a*-Si:(H,O,N) and the parameters α and β of beryl are shown in Fig. 4. The H_t untrapping activation energy of *a*-Si:(H,O,N) is $E_\alpha = 0.56$ eV and the preexponential frequency factor $\alpha_0 = 1.5 \times 10^9$ s^{-1}. It is clear that both parameters α and β of beryl obey the Arrhenius law with

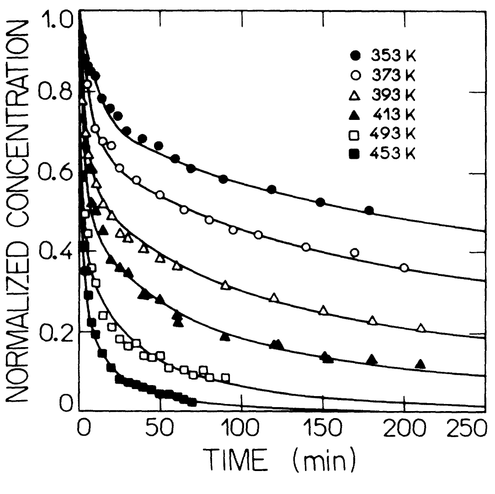

FIG. 3. Numerical integration results (solid lines) adjusted to the experimental points of the isothermal $[H_t]$ decay in beryl (Ref. 2).

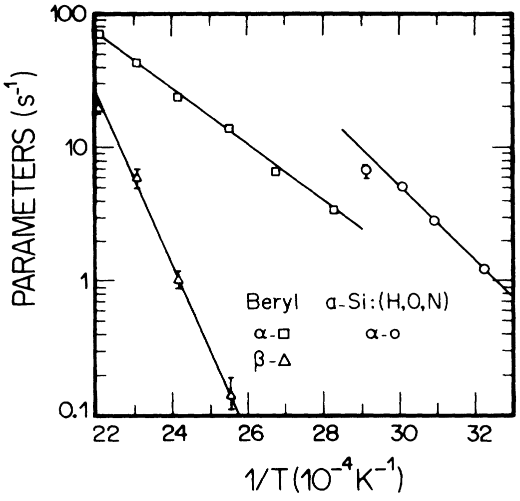

FIG. 4. Arrhenius law applied to the parameters α and β for beryl and α for *a*-S:i(H,O,N).

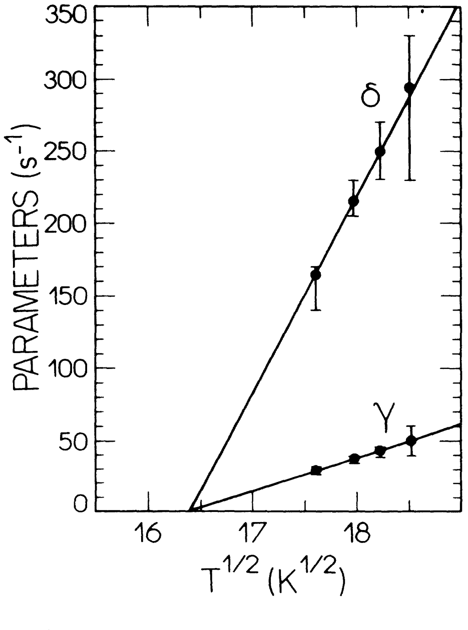

FIG. 5. $T^{1/2}$ behavior observed for the γ and δ parameters of $[H_t]$ in *a*-Si:(H,O,N). The common cutoff temperature is $T_0 = 269$ K.

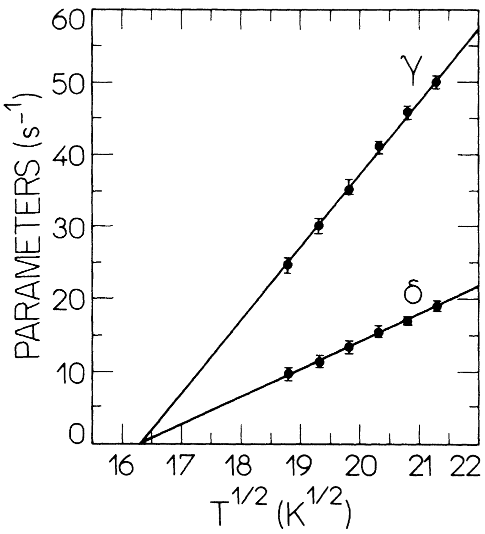

FIG. 6. $T^{1/2}$ behavior observed for the γ and δ parameters of $[H_t]$ in beryl. The common cutoff temperature is $T_0=266$ K.

activation energies equal, respectively, to $E_\alpha=0.42$ eV and $E_\beta=1.51$ eV, and preexponential frequency factors $\alpha_0=3.33\times10^6$ s^{-1} and $\beta_0=3.5\times10^{18}$ s^{-1}.

Figure 5 shows the correlation of γ and δ for $[H_t]$ in *a*-Si:(H,O,N) with $T^{1/2}$. The observed correlation is linear, with a common cutoff temperature $T_0=269$ K for all parameters. Thus γ and δ are linear functions of $T^{1/2}-T_0^{1/2}$.

The temperature dependence for γ and δ is observed over a very small temperature range. It is easy to check that $\ln\gamma$ and $\ln\delta$ vary linearly with $1/T$, too, and well within the quoted error bars. The temperature dependence is not established strongly enough to discard a more classical Arrhenius behavior, since the accuracy of the measurements is not sufficient to retain a $T^{1/2}$ dependence exclusively.

The dependence of γ and δ for $[H_t]$ in beryl on $T^{1/2}$ is shown in Fig. 6. The behavior is again linear, with cutoff temperature $T_0=266$ K, and here again γ and δ are linear functions of $T^{1/2}-T_0^{1/2}$.

In Fig. 4 it is shown that the parameter β, adjusted to the kinetics of $[H_t]$ in beryl, obeys the Arrhenius law. The parameter β is related to the recombination process of R and H_f. The high activation energy suggests that the irradiation produced an R radical from the radiolysis of H_2O, namely, energy OH^-. Therefore, the activation energy is probably equal to the energy necessary for the ionization of OH^- into $OH+e^-$ before the reaction $OH+H_f\rightarrow H_2O$ takes place. An alternative possible reaction is $OH^-+H_f\rightarrow H_2O^-\rightarrow H_2O+e^-$.

IV. TEMPERATURE DEPENDENCE OF δ AND γ

The hydrogen atom in silicon is trapped by an oxygen defect because no H_t EPR signal was observed in oxygen-free silicon. The trapping of atomic hydrogen changes the structure of the oxygen defect. This change of structure requires energy, giving rise to a potential barrier E_b for trapping atomic hydrogen. The untrapping of atomic hydrogen requires an activation energy E_α.

The calculation of the interaction of atomic hydrogen in crystalline Si by the completely neglected differential overlap (CNDO) method showed that there is an energy difference between tetrahedral and hexagonal sites of 0.052 eV. The relaxation of host atoms near the hydrogen alters this picture, however. There is very little change of energy for the hydrogen in the tetrahedral site if four neighboring Si atoms are moved, but if the six Si atoms adjacent to the hexagonal site relax outwards by only 1% of a lattice spacing, the energy of the hydrogen in the hexagonal position drops to a very similar energy to the tetrahedral one.[23] Although *a*-Si has quite different structure from crystalline Si, it is reasonable to assume that the interaction of atomic hydrogen with a neighboring Si atom is the same. Thus we assume that atomic hydrogen can move through the *a*-Si network almost as a free particle with effective mass m_H $(m_H<m_p+m_e)$.

Here we assume that the free H_i^0 acquires, through collisions with the atoms of the network, speeds varying from 0 to high values, according to the free-particle Maxwell speed distribution

$$dN_v=\frac{4N}{\sqrt{\pi}}\left[\frac{m_H}{2kT}\right]^{3/2}v^2\exp\left[-\frac{m_Hv^2}{2kT}\right]dv\ , \qquad (3)$$

where N is the concentration of H_f atoms, v is the speed, and T is the absolute temperature. Consider N atoms per unit volume traveling in the network with speeds between v and $v+dv$. By assuming that each collision with atoms N' removes one H_f atom, we may evaluate the decreasing rate of N between t and $t+dt$ according to

$$dN=-PN\,dx\ , \qquad (4)$$

where $P=\sigma N'$, σ denotes a cross section, and $dx=v\,dt$. The rate of concentration change for all speeds is then given by the sum over all dN_v, giving

$$\frac{dN}{dt}=-\int_{\text{all}}\sigma vN'\,dN_v\ . \qquad (5)$$

To calculate the integral of Eq. (5), we need to know the dependence of σ on v. One possible source of dependence of σ on v is the structure of the trapping defect.

The H^0 in *a*-Si(H,N,O) is trapped in two sites as showed by Pontuschka *et al.*[1] One H^0 is associated with a sharper EPR line of about 3 G of linewidth, and the other is associated to a broader EPR line of about 13 G of linewidth. The sharp line is saturated at very low microwave power. This H^0 could be assigned to H^0 trapped in the large cavities of Si (about 20 Å) with the boundary formed by Si-bonded hydrogen pointed to the outside of the cavity and with the dangling bonds to the inner part.[24] This H^0 is probably trapped in the field of Si—O—Si bonds pointed to the inner part. The combination of H^0 with the dangling bonds and with oxygens of Si—O—Si bonds is prevented due to the high reaction energies required. The broader 13-G linewidth was the subject of the Pontuschka *et al.*[1] kinetics study, where the sharper line was eliminated measuring with high enough microwave power. The strong broadening suggests high spin-lattice relaxation. This is possible if H^0 is trapped in a site with short-distance neighbors, i.e., a site with local structure similar to that found in crystalline Si.

In crystalline Si it was shown that the $4O_i$ defect is stable.[25] This defect is formed by the occupation by atomic oxygens, of the four empty sites of tetrahedral symmetry at the vertices of the cube of side $a/2$. The other vertices of this cube are occupied by four Si atoms. The center of this cube has tetrahedral symmetry and is also empty. A possible trapping defect of atomic hydrogen is the empty site at the center of the cube.

Energy E_b is required to relax the O_i and Si atoms outward to allow the introduction of atomic hydrogen. In the inner part of the $4O_i$ defect, the interaction between the atomic hydrogen atom with O_i and Si atoms, through London dispersion forces, relax these atoms close together. This relaxation traps the atomic hydrogen with an energy E_α. The energy diagram for this defect is sketched in Fig. 1.

If the kinetic energy of H^0 is smaller than E_b, it has probability that H^0 will surpass the potential barrier, and then the trapping cross section becomes negligible. However, because of the phonon distribution, it is possible to assume that the reaction occurs according to the Arrhenius scheme. In this case the probability of trapping is roughly given by $\sigma=\sigma_0 c_0 \exp(-\Delta E_v/kT)$ for $v<v_b$, where c_0 is a constant $(0\le c_0\le 1)$ and $\Delta E_v=\frac{1}{2}mv_b^2-\frac{1}{2}mv^2$. The velocity v_b is given by $(2E_b/m_{\mathrm{H}})^{1/2}$ and corresponds to the velocity at which H^0 surpasses the barrier of potential.

If $v>v_b$, H^0 can be trapped only if there is a suitable mechanism for energy loss.[26] All the sublevels of the H^0 trapping potential energy are vibrational levels. Even for particles with kinetic energy higher than E_b, there are vibrational levels along the H^0—O_i or H^0—Si directions (tracked lines in Fig. 1). The atomic hydrogen can jump from one state to another with the help of a single phonon. Since the probability of one phonon transition is substantial, such a transition enables H^0 to be trapped. The motion of the descent of H^0 down the ladder of excited states, losing its energy by the successive emission of single phonons, is so rapid compared with the rate at which H^0 is trapped that the corresponding delay may be neglected. Also, this energy-losing process is faster than the time by which H^0 can surpass the defect. Thus, for $v>v_b$, we assume σ to be independent of v. Assuming that σ is continuous, we get $\sigma(v)=\sigma_0$.

Using Eq. (3), and the dependence of σ on v as assumed above, we obtain the rate equation

$$\frac{dN}{dt}=-\frac{1}{\sqrt{\pi}}N'N2\sigma_0 v_b f(x) , \tag{6}$$

where

$$f(x)=x\left[1+\frac{1}{x^2}+\frac{c_0}{2x^3}\right]e^{-1/x^2}$$

and $x=\sqrt{kT/E_b}$.

The limit value for high temperature or negligible potential barrier is

$$\frac{dN}{dt}=-\sigma_0\left[\frac{8kT}{\pi m_{\mathrm{H}}}\right]^{1/2}NN' , \tag{7}$$

showing a $\sqrt{T}$ dependence for the rate constant. The limiting value for low temperature or high potential barrier is, for $c_0\neq 0$,

$$\frac{dN}{dt}=-\sigma_0 c_0\left[\frac{2E_b}{\pi m_{\mathrm{H}}}\right]^{1/2}\frac{E_b}{kT}e^{-E_b/kt}NN' , \tag{8}$$

showing a $e^{-E_b/kt}/T$ dependence for the rate constant, and for $c_0=0$,

$$\frac{dN}{dt}=-\sigma_0\left[\frac{8E_b}{\pi m_{\mathrm{H}}}\right]^{1/2}\left[\frac{E_b}{kT}\right]^{1/2}e^{-E_b/kt}NN' , \tag{9}$$

showing a $e^{-E_b/kt}/T^{1/2}$ dependence for the rate constant.

Figure 7 shows the dependence of $f(x)$ on x for $c_0=0$ and 1. There are two intervals for x values where $f(x)$ can be fit to a linear function of the form $p(x-x_0)$. For $c_0=0$ we have for the interval $0.6<x<1.1$, $p=1.51$ and $x_0=0.51$, and for the interval $1.3<x<4$, $p=1.17$ and $x_0=0.32$. For $c_0=1$ we have for the interval $0.5<x<0.9$, $p=1.7$ and $x_0=0.43$ and for the interval $1.3<x<2$, $p=1.04$ and $x_0=0.07$.

The linear part of $f(x)$ supports the empirical observation of $(\sqrt{T}-\sqrt{T_0})$ behavior of the parameter γ. Otherwise, only this part of the dependence of γ and T is not enough for the determination of E_b.

The empirically determined function for $\delta=\delta_0(\sqrt{T}-\sqrt{T_0})$ is similar to that observed for γ. Thus we would like to apply the present analysis to δ by assuming a potential barrier for the reaction $H_f+H_f\rightarrow H_2$. Of course, for free atoms there is no po-

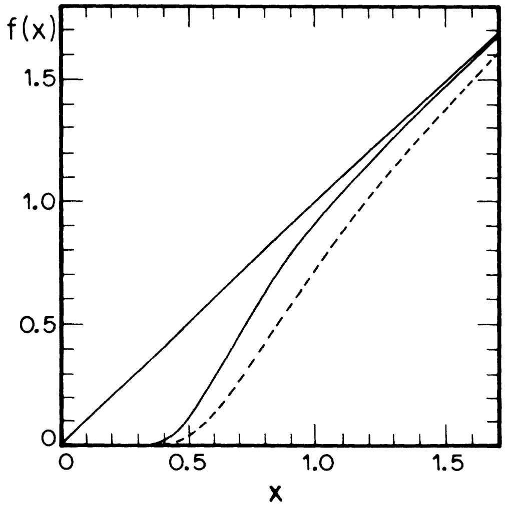

FIG. 7. $f(x)$ function vs x for $c_0=0$ (dashed line) and $c_0=1$ (solid line). The straight line is the limit of the function $f(x)\rightarrow x$ for $x\gg 1$.

tential barrier. However, H_f is under the effect of the atoms of the material network. These effects, which include dispersion and exchange interactions, could inhibit formation of a H_2 molecule, in a similar way as observed in the inhibition of formation of O_2 in crystalline Si.[25] This inhibition could explain the assumption of a potential barrier for the formation of H_2.

Here we assumed an Arrhenius fit to β, although the suggested behavior was $e^{-E_\beta/kt}/T$ due to the high E_β value. The error introduced in E_β by the Arrhenius plot is small, because the $1/T$ function changes slower than $e^{-E_\beta/kT}$. In fact, the log plot of (x) is a sum of $\ln T$ and E_β/kT. The $\ln T$ term introduces a contribution which changes from 5.87 (353 K) to 6.12 (453 K) with about 4% of variation. This variation is smaller than the error in the determination of β, and the term $\ln T$ can be neglected.

V. CONCLUSIONS

The numerical Runge-Kutta method, applied to a system of differential equations describing the isothermal decay kinetics of $[H_f]$ in x-irradiated *a*-Si(H,O,N) and uv-irradiated natural beryl, led to conclusions which can be summarized as below.

(a) The hydrogen removal mechanism which occurs on heating *a*-Si:H is processed through the irreversible formation of molecular H_2, in good agreement with the assumption proposed by Pontuschka *et al.*[1] In this work it is assumed that the reaction $H_f+H_f \rightarrow H_2$ has a small activation energy derived from the interaction of H^0 with the network.

(b) The untrapping of H_t in *a*-Si:(H,O,N) obeys the Arrhenius law with activation energy $E_\alpha=0.56$ eV and preexponential factor $\alpha_0=1.5\times10^9$ s^{-1}. The present activation energy is similar to the diffusion of the atomic hydrogen activation energy of 0.48 eV found in single-crystal silicon.[27]

(c) The recombination parameter β is negligible for H_f in *a*-Si:(H,O,N) (it is unlikely that the radiolytic H_f will be recovered in the original structure).

(d) The recombination parameter β is not negligible for H_f in beryl, a fact which minimizes the loss of hydrogen by the sample.

(e) Both α (untrapping) and β (recombination) parameters obey the Arrhenius law for beryl with activation energies equal, respectively, to $E_\alpha=0.42$ eV and $E_\beta=1.51$ eV and preexponential factors equal, respectively, to $\alpha_0=3.3\times10^6$ s^{-1} and $\beta_0=3.5\times10^{18}$ s^{-1}. The recombination of H_f in beryl is possibly processed through the reaction

$$H_f+OH^- \rightarrow H_2O+e^- ,$$

and justifies the high $E_\beta=1.51$ eV activation energy.

(f) The parameters γ (retrapping) and δ (H_2 formation) were found to fit a function proportional to $T^{1/2}-T_0^{1/2}$ with $T_0=269$ K for H_f in *a*-Si:(H,O,N) and $T_0=266$ K in beryl. It was shown that this function can be assigned to the linear part of the $f(x)$ function derived from free-particle distribution of speeds attributed to H_f and the potential barrier for retrapping and H_2 formation.

As the dangling-bond population was minimized by bonded hydrogen atoms in *a*-Si:(H,O,N), it is reasonable to suppose that a neutral intersticial atomic hydrogen is able to diffuse by a length at least greater than the distance to its nearest neighbors. This gives rise to a preliminary diffusion with a different activation energy expected than that reported for the motion of bonded hydrogen. If the number of nonpassivated dangling bonds is sufficiently small, we expect that the probability of the occurrence of extensive diffusion as a precursor of the reaction $H^0+H^0 \rightarrow H_2$ turns out to be important in the system.

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