EXPERIMENTAL STUDIES OF HYDROGEN MOTION IN HYDROGENATED AMORPHOUS SILICON AND GERMANIUM

J. SHINAR, S. MITRA, AND X.-L. WU
Ames Laboratory - USDOE and Physics Department,
Iowa State University
Ames, IA 50011, USA

R. SHINAR
Microelectronics Research Center
Iowa State University
Ames, IA 50011, USA

ABSTRACT. An infrared and secondary ion mass spectrometry study of H diffusion in undoped, rf sputtered multilayered hydrogenated/deuterated amorphous silicon (a-Si:H) and germanium (a-Ge:H) is reported. The results indicate that in a-Si:H, the long range motion of atomic H is suppressed by a microvoid content exceeding a critical value associated with an initial SiH$_2$ and SiH$_3$ density $N_{do}$ \approx 7\% at.\%. Qualitatively similar behavior is observed in a-Ge:H. In a-Si:H, the diffusion constant is strongly power-law time dependent slightly above the threshold (exponent $\alpha \approx 0.75\pm0.15$). In a-Ge:H containing essentially only bulk mono Ge-H centers, $\alpha = 0.23$. The implications of these results to the nature of the diffusion process in general and the intrinsic defects contributing to it in particular is discussed.

1. Introduction

Thin film hydrogenated amorphous silicon (a-Si:H) based alloys and multilayers have matured in various technological areas in recent years.\(^1\) Conceptually, the system is often regarded as the prototypical distorted tetrahedral network. As such, fundamental issues concerning the structural and electron dynamics of this system,\(^2\) the nature of the dominant defect,\(^3\) and the motion of hydrogen are still not satisfactorily resolved.\(^4\) This work offers new insight into the latter two issues.

Carlson and Magee\(^5\) (CM) first studied long range H motion in a-Si:H deposited by glow discharge decomposition of silane (gd films). Using secondary ion mass spectrometry (SIMS), they determined the activation energy $E_a=1.53eV$ and prefactor $A_0=0.012cm^2/s$ by profiling the smeared interfaces of a-Si:H/a-Si:D/a-Si:H multilayers annealed over widely varying periods in the temperature range 250\(^\circ\)C to 400\(^\circ\)C, from 7 days at 250\(^\circ\)C to 17 mins at 400\(^\circ\)C. Subsequent detailed SIMS studies were reported by the Xerox group\(^4,6\) on mostly p-doped, some n-doped, and compensated gd films annealed at T<275\(^\circ\)C. They showed that the diffusion is faster in n doped, and much faster in p doped films, due mostly to an increasing prefactor. The prefactor actually

573

appeared to be directly proportional to the measured ESR spin density of the films. In addition, the results indicated that the diffusion constant decreases with time, in a power-law dependence given by

$$D(t) = D_{oo}(\omega t)^{-\alpha} \quad (1)$$

where \(\omega\) is the H attempt frequency. Kakalios et al.\(^6\) initially assumed that \(D_{oo}\) is temperature dependent. The value of \(\alpha (\approx 0.2\) at 480K) was suggested to explicitly depend on the temperature in the following manner

$$\alpha = 1 - T/T_o \quad (2)$$

where \(T_o = 600\)K is the characteristic energy width of the exponential hopping distribution in the dispersive transport of hydrogen. Reanalysis of the previous results by Jackson\(^8\) suggested, however, that \(D_{oo}\) is actually temperature independent. He showed that the diffusion constant following annealing at times necessary to diffuse a constant distance \(L, D(t_f),\) is thermally activated due to the dependence of \(\alpha\) and \(t_f\) on \(T\). All of the previous studies involved gd films essentially devoid of SiH\(_2\) and SiH\(_3\) bonds which are associated with microvoids. The new results described and discussed in this paper involve rf sputter-deposited films\(^9,10\) of a-Si:H and a-Ge:H, indicating that when the microvoid content in a-Si:H corresponds to an initial di- and tri-H density \(N_{do}\) exceeding \(7^{+1}\) at.\%, the long range motion of atomic H and D is effectively suppressed. In films of \(N_{do}\) values somewhat below this value, the diffusion is highly anomalous, with the diffusion constant exhibiting a strong power-law time dependence, \(\alpha \approx 0.75 \pm 0.15\). The results on a-Ge:H are qualitatively similar, but the exponent \(\alpha\) in films of bulk mono-H bonding only is lower, \(-0.23\), and the diffusion is faster. These new observations are discussed in relation to diffusion models involving H motion mediated by the migration and annihilation of bulk intrinsic defects,\(^3\) and the presence of an exponential distribution of hydrogen site energies. While neither is ruled out, some problems associated with both scenarios are pointed out.

2. Experimental Procedure

a-Si:H/D/H and a-Si:H/(H,D)/H multilayers 1-2\(\mu\)m thick were deposited by 50-600W rf sputtering of a 6" diameter polycrystalline Si target, \(-1\)" above the substrate, in a mixture of about 10mtorr Ar, \(-1\)mtorr H\(_2\), and D\(_2\) (see Table I). The temperature of the unheated substrates was estimated at \(120-150\)\(^\circ\)C during deposition.\(^9\) Detailed descriptions of the deposition processes may be found elsewhere.\(^9,11\) a-Si:H/D/H multilayers were fabricated by turning one gas (D\(_2\) or H\(_2\)) on before turning the other (H\(_2\) or D\(_2\)) off at the interfaces. a-Si:H/(H,D)/H multilayers were fabricated by simply adding a partial pressure of D\(_2\), equal to about 30-50\% that of the H\(_2\), during the deposition of the middle layer. The films were annealed at temperatures \(270<\)T<\(355\)\(^\circ\)C in evacuated sealed pyrex tubes.

Films of a-Ge:H were prepared in a second rf sputtering system, by similarly sputtering a 6" polycrystalline Ge target at 300W 3" above the grounded substrates at a temperature estimated to be \(-75\)\(^\circ\)C.

The total Si-bonded H content of the films \([H_t]\) was determined from the 640cm\(^{-1}\) IR wagging mode absorption peak using the absorption coefficient