

Oxidation of Hafnium and Diffusion of Hafnium Atoms in Hexagonal Close-Packed Hafnium; Microscopic Investigations by Perturbed Angular Correlations

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Time-differential perturbed angular correlation (TDPAC) studies in hafnium metal ($\sim 5\%$ Zr) have been carried out at different temperatures. It is found that hafnium metal on heating at 873 K continuously for two days in air, transforms partially and abruptly to HfO_2 while no component of oxide has been observed for heating up to 773 K and during initial heating at 873 K for 1 day. This result is strikingly different to that expected from the Arrhenius theory. Also, a strong nuclear relaxation effect has been observed at 873 K due to rapid fluctuation of hafnium atoms in hexagonal close-packed (hcp) hafnium. At this temperature, $\sim 45\%$ probe nuclei experience static perturbation due to monoclinic HfO_2 , $\sim 50\%$ experience fluctuating interaction, and $\sim 5\%$ produce static defect configuration of hcp hafnium. With lowering of temperature, defect configurations of hafnium increase at the cost of fluctuating interaction. An almost total fluctuating interaction observed in hcp hafnium at a temperature much lower than its melting point is another interesting phenomenon.

Key words: Hf Metal; Transformation to HfO_2 ; Diffusion of Hf; TDPAC(T).

1. Introduction

The possibility of application of high-permittivity dielectric HfO_2 ($k \sim 20$) to replace the conventional SiO_2 gate dielectric in future generations metal–oxide–semiconductor field-effect transistors has generated recent interests in HfO_2 material [1–4]. A recent observation of magnetism in thin film HfO_2 [5] has also grown interest to understand this magnetism where both the Hf^{4+} and O^{2-} ions are non-magnetic and no long-range magnetic ordering is expected normally in HfO_2 . On the other hand, our very recent studies [6] by time-differential perturbed angular correlation (TDPAC) do not reveal any magnetic ordering in thin film HfO_2 . The aim of present TDPAC studies is to look for the oxidation temperature of hafnium from the microscopic behaviour of hafnium metal with temperature under heating in air. The hafnium metal is known to have a strong affinity for oxygen and, therefore, is expected to be easily oxidized on heating in air. The TDPAC signals corresponding to hexagonal close-packed (hcp) Hf and monoclinic HfO_2 are clearly different and help to discriminate the two components in the sam-

ple. In the present report, temperature dependent studies in hcp Hf metal have been carried out in the temperature range 298–873 K and from these measurements, two important conclusions have been drawn. First, it is shown that Hf metal transforms abruptly to monoclinic HfO_2 at 873 K on prolong heating for two days in air while there was no oxide component up to 773 K and during initial heating at 873 K. This behaviour contradicts the Arrhenius theory. A gradual increase of growth rate of oxide with temperature is expected. It is also found that when Hf metal was heated at 873 K for a sufficiently long time, the static perturbation due to crystalline hcp Hf vanishes and a strong time-dependent spin relaxed component due to fluctuation of Hf atoms is observed. An almost completely fluctuating signal in Hf metal at 873 K is the second unexpected interesting phenomenon where the melting point of Hf (2500 K) is much higher than 873 K. At this temperature, no static frequency component due to hcp Hf has been observed. This indicates that at a temperature much below of its melting point a metal can exist where the atoms fluctuate randomly from an occupied site in the crystal to a vacant site and this

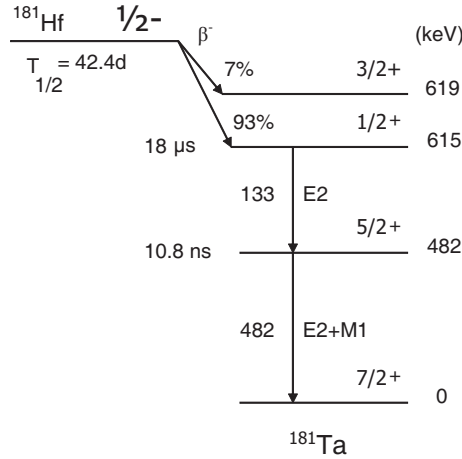


Fig. 1. Partial decay scheme of ^{181}Hf .

happens so rapidly that no crystal structure is exhibited.

2. Experimental Details

In time-differential perturbed angular correlation technique [7], the nuclear quadrupole interactions (NQI) between the quadrupole moment of the ^{181}Ta nucleus and the extra-nuclear electric field gradient generated at the nuclear site by the surrounding environment are studied. The probe ^{181}Hf nucleus which undergoes β^- decay to ^{181}Ta has been used for present studies. Due to nuclear quadrupole interaction, the 133–482 keV $\gamma-\gamma$ angular correlation of ^{181}Ta passing through the 482 keV level (Fig. 1) is perturbed. The perturbed angular correlation of the 133–482 keV cascade is given by

$$W(\theta, t) = \exp(-t/\tau) [1 + A_2 G_2(t) P_2(\cos \theta) + A_4 G_4(t) P_4(\cos \theta)].$$

Here, θ is the angle between the detectors, A_2 , A_4 are angular correlation coefficients of the $\gamma-\gamma$ cascade, and τ is the mean lifetime of the intermediate level. The nuclear structure parameters A_2 and A_4 depend on the spin sequence of the nuclear levels involved in the cascade and the γ -ray multiplicities. The values of A_2 and A_4 for the 133–482 keV cascade in ^{181}Ta are -0.288 and -0.076 [7]. $G_2(t)$ and $G_4(t)$ describe the extra nuclear perturbations in the medium. Time t is the time difference between the start 133 and stop 482 keV

γ -rays. The perturbation function $G_2(t)$ and $G_4(t)$ can be obtained from the ratio of coincidence counts of the two γ -rays at angles 180° and 90° [7].

The perturbation function $G_k(t)$ can be written as $G_k^{\text{static}}(t) = \sum_{n=0}^N S_{kn}(\eta) \cos(\omega_n t)$, where the S_{kn} coefficients are functions of source orientation and are different for single crystal and polycrystalline materials [7]. N depends on the spin I of the intermediate nuclear level of the $\gamma-\gamma$ cascade. In the present case ($I = 5/2$), the perturbation function for a polycrystalline sample and for $k = 2$ is given by

$$G_2^{\text{static}}(t) = \left[\sum_{n=0}^3 S_{2n}(\eta) \exp(-n\delta t) \cos(\omega_n t) \right]. \quad (1)$$

The exponential terms account for a Lorentzian frequency distribution due to imperfection in the crystal. The three frequencies ω_1 , ω_2 , and ω_3 correspond to transitions between the sublevels of the intermediate level with $I = 5/2$. These sublevels appear due to the interaction of the nuclear quadrupole moment with the local electric field gradient (hyperfine splitting), and transitions between different m sublevels modulate the angular correlation. Without this interaction, the m sublevels become degenerate and no perturbation of angular correlation is obtained. The quadrupole frequency is related to the largest diagonal component V_{zz} of the electric field gradient tensor in the principle-axis coordinate system by $\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$. Here, Q is the nuclear electric quadrupole moment of the intermediate 482 keV level ($Q = 2.35\text{b}$) [8]. For an axially symmetric electric field gradient ($\eta = 0$), ω_Q is related to ω_1 , ω_2 , and ω_3 as $\omega_Q = \omega_1/6 = \omega_2/12 = \omega_3/18$.

In general, more than one interaction frequency is present in a sample due to the existence of either various inequivalent sites within the same compound or a mixture of different compounds in the sample. The corresponding perturbation function can be written as $G_2(t) = \sum_i f_i G_2^i(t)$, where f_i is the fraction of the i th component.

Time-dependent quadrupole interactions in solids are mostly due to atomic motion near to the probe atom. This arises due to the instantaneous change in the electric field gradient at the nuclear site caused by fluctuation of the atoms surrounding the probe atom. The effect of the nuclear spin relaxation caused by jumping atoms on the angular correlation is most appropriately described by Blume's stochastic theory [9, 10]. The analysis of experimental data is frequently based

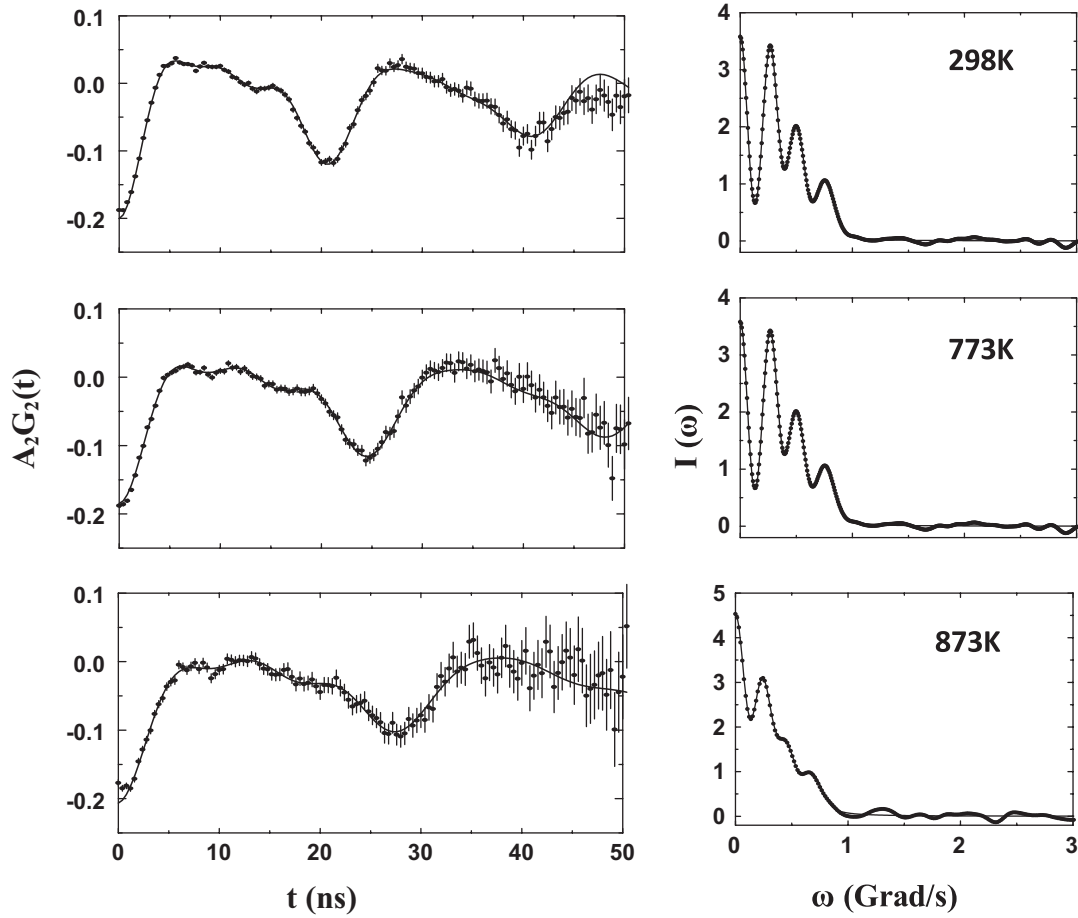


Fig. 2. TDPAC spectra in Hf metal at room temperature, 773 and 873 K. Left: time spectrum, right: corresponding Fourier transforms. The spectrum at 873 K (after heating for one day) shows both static and time-dependent components.

on an approximation of the Blume theory with a single relaxation parameter λ_2 and is given by

$$G_2(t) = G_2^{\text{static}} \exp(-\lambda_2 t). \quad (2)$$

Here, G_2^{static} is the static quadrupole interaction (QI) as written above. In the case of overbarrier diffusion with an Arrhenius relation of the jump rate $w = w_0 \exp(-E_A/kT)$ (E_A is the activation energy) and slow fluctuations where the jump rate is very small compared to the centre of the static distribution of quadrupole frequencies, the relaxation constant is given by [11]

$$\lambda_2 = \lambda_2^- \exp(-E_A/kT) \quad (3)$$

for the slow-fluctuation lower-temperature regime.

Fast fluctuations are adequately described by (2) if several jumps occur within one precession period. In the fast-fluctuation regime the function G_2^{static} is determined by the time average of the interaction. For vanishing time average, $G_2^{\text{static}} = 1$ and the relaxation parameter λ_2 corresponds to the Abragam and Pound spin relaxation constant [12]. In this case, the relaxation constant is given by [12]

$$\lambda_2 = \lambda_2^+ \exp(E_A/kT) \quad (4)$$

for the fast-relaxation higher-temperature regime.

The TDPAC studies have been performed in a polycrystalline hafnium metal wire with a nominal zirconium concentration of ~ 5 wt %. A small piece of natural Hf metal (~ 2 mg) procured from M/S Alfa Aesar was irradiated by thermal neutrons in the CIRUS

reactor, Mumbai, to produce the active ^{181}Hf . For TDPAC measurements, a four detector spectrometer with BaF_2 detectors has been used. From the four coincidence spectra (two at 180° and two at 90°), the perturbation function $G_2(t)$ has been found as described earlier [13]. For measurement above room temperature, a small resistive furnace has been used. The sample was taken in a quartz tube and was put inside the furnace placed at the centre of the four detectors. The sample is allowed to be heated in air during measurements at higher temperatures.

3. Results and Discussion

The TDPAC spectrum in Hf metal (Fig. 2) at room temperature gives two frequency components. The present Hf metal sample in the form of Hf wire shows ‘texture effects’ which means the electric field gradients are not randomly oriented as expected for a polycrystalline sample. The TDPAC spectra are, therefore, fitted with free S-coefficients (1). The fitted values of quadrupole frequency and asymmetry parameter for the main component are found to be $\omega_Q = 50.4(1)$ Mrad/s, $\eta = 0.18(1)$ with a value of $\delta = 5.1(3)\%$. These are in good agreement with the earlier reported results [14] and this component corresponds to the hcp lattice structure of Hf metal. A damping in the time spectrum ($\delta \sim 5\%$), and a non-zero value η is due to the presence of zirconium impurity (~ 5 wt %) [15]. Values of quadrupole frequency and asymmetry parameter for the weak component have been found to be $\omega_Q = 43.8(7)$ Mrad/s and $\eta = 0.65(3)$ with $\delta = 0$. This signal arises possibly due to trapping of an oxygen atom in the interstitial site of the Hf lattice [16]. It has been found that up to 773 K, the component fractions do not change appreciably (Tab. 1) and the spectra remain almost unchanged (Fig. 2) in the temperature range 298–773 K.

Interestingly, the Hf metal sample when heated at 873 K for one day produces a fluctuating signal at the cost of the static frequency component due to hcp Hf (Fig. 2). The presence of a time-dependent signal at this temperature is clearly observed from the Fourier transformed spectrum. In the Fourier representation, the three Fourier peaks (ω_1 , ω_2 , and ω_3) with decreasing intensity characterize the pure static interaction while an exponential characterizes the time-dependent interaction. When there is both static and time-dependent interaction, the three Fourier peaks ap-

Table 1. Results of TDPAC measurements in Hf metal at different temperatures.

Temp. [K]	comp.	ω_Q [Mrad/s]	η	δ [%]	f [%]
298	1	50.4(1)	0.18(1)	5.1(3)	91(2)
	2	43.8(7)	0.65(3)	0	9(2)
473	1	48.1(2)	0.18(2)	4.2(4)	89(2)
	2	41.3(9)	0.64(4)	0	11(2)
573	1	47.2(2)	0.17(3)	4.2(5)	89(3)
	2	41(1)	0.55(6)	0	11(3)
673	1	45.7(2)	0.16(3)	4.7(4)	90(3)
	2	40(1)	0.59(5)	0	10(3)
773	1	42.5(2)	0.20(3)	4.8(5)	90(3)
	2	36(1)	0.52(10)	0	10(3)

pear on an exponential background. However, in this case, the static frequency component has been found to be 82% while the fluctuating component comes out to be 18%. No other static frequency component is found to be present here. This result is interesting and indicates clearly that in the heating at 873 K for one day, a significant fraction of Hf atoms in the Hf crystal fluctuates randomly from an occupied site to a vacant site generated at this temperature. Since no signal due to HfO_2 or oxygen deficient HfO_{2-x} is found to be present, the question of fluctuation due to the oxygen atom does not arise. For the fluctuating component, a value of relaxation constant $\lambda_2 = 29(5)/\mu\text{s}$ has been obtained using the Abragam and Pound relaxation theory [12] given by $A_2(t) = A_2(0)\exp(-\lambda_2 t)$.

When the heating of the sample at 873 K goes on after one day, the spectrum is found to be changing continuously due to a transformation in the sample. It is found that after heating for two days a thermal equilibrium is reached at this temperature. Here, the spectrum is found to be changed completely (Fig. 3) and no static frequency component due to hcp Hf appears any more, but a strong time-dependent relaxed component is observed along with a new static frequency component. The spectrum $A_2 G_2(t)$ and its Fourier transform clearly show the time-dependent signal. The static quadrupole interaction in this case corresponds to $\omega_Q = 115.6(6)$ Mrad/s and $\eta = 0.418(9)$. This component is assigned to be the monoclinic HfO_2 by comparing with the corresponding values of ω_Q and η reported earlier [17]. The values of ω_Q and η in monoclinic HfO_2 were found to be 123.0(5) Mrad/s and 0.340(3) [17], respectively, at room temperature. It was found also that the value of ω_Q decreases and η increases with temperature [17]. The component HfO_2 is formed at 873 K due to heating of the Hf metal in air

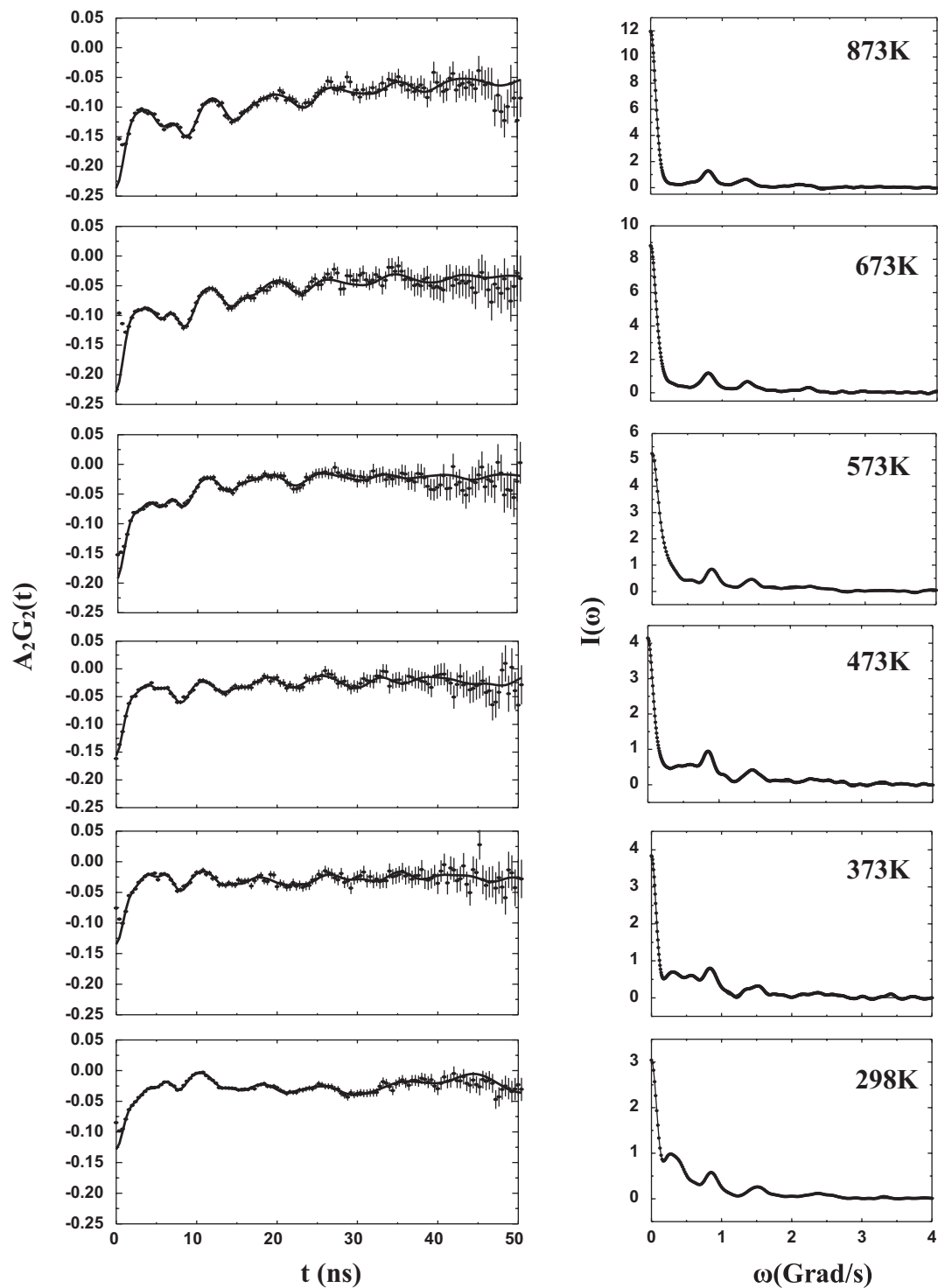


Fig. 3. TDPAC spectrum in Hf metal after continuous heating for two days in air at 873 K. The spectra at different lower temperatures are also shown. Left: time spectrum; right: corresponding Fourier transforms.

Table 2. Results of TDPAC measurements in Hf metal at 873 K and lower temperatures.

Sample Temp. [K]	comp.	ω_Q [Mrad/s]	η	δ [%]	f^{static} [%]	f^{relax} [%]	λ_2 [μs^{-1}]
873 (for heating up to 1 day)	1	37.1(3)	0.26(2)	8(1)	82(2)		
	2					18(2)	29(5)
873 (after heating for 2 days)	1	113.6(6)	0.426(9)	6.0(7)	45(3)		
	2	58(1)	0.77(4)	0	5(2)		
	3					50(3)	40(1)
673	1	117.0(7)	0.39(1)	7(1)	47(3)		
	2	56(2)	0.64(9)	0	3(2)		
	3					50(3)	74(2)
573	1	120(1)	0.41(2)	7(1)	44(3)		
	2	74(4)	0.56(11)	0	2(2)		
	3					54(3)	160(5)
473	1	127(1)	0.29(2)	8(1)	51(5)		
	2	56(1)	0.50(3)	0	9(2)		
	3	76(1)	0.45(4)	0	9(2)		
	4					31(5)	133(7)
373	1	129(1)	0.33(2)	6(2)	46(3)		
	2	70(1)	0.56(3)	0	12(2)		
	3	53(1)	0.33(4)	0	13(1)		
	4	38(1)	0.36(6)	0	12(2)		
	5					17(1)	101(11)
298	1	129.3(8)	0.36(1)	7(1)	47(2)		
	2	33.2(3)	0.36(2)	0	24(1)		
	3	42.0(5)	0.49(2)	0	15(1)		
	4					14(1)	70(8)

for two days. Heating of Hf metal at 773 K or at 873 K up to one day produces no component due to HfO_2 . This result is interesting considering the fact that the growth rate of oxide with temperature does not follow the Arrhenius behaviour. In fact, no temperature dependence of HfO_2 growth rate has been found in the heating of Hf metal. The oxide appears abruptly at 873 K. In the earlier study [4], however, hafnium oxide growth rate was found to be following the Arrhenius behaviour when the Hf metal was heated at higher temperatures. The fast relaxed component that appears at 873 K after the sample was heated for two days is found to be $\sim 50\%$ with a value of $\lambda_2 = 40(1) \mu\text{s}^{-1}$ while the static frequency component due to HfO_2 has been found to be 45%. The remaining 5% (Tab. 2) can be attributed to a defect configuration of hcp Hf since its quadrupole frequency is closer to that of hcp Hf. The strong fluctuating signal can again be attributed to diffusion of Hf atoms, and hopping of oxygen can be ruled out as no signal due to oxygen deficient HfO_{2-x} is observed at reduced temperatures. The quadrupole frequency corresponding to HfO_{2-x} is expected to be closer to HfO_2 as found from earlier measurement [4]. Here, the Hf atoms fluctuate so rapidly throughout the lattice that only a fluctuating rather than a static elec-

tric field gradient is observed. This can be supported also from our measurements at lowered temperatures as discussed below. As temperature is gradually reduced, more and more defect signals of Hf appear at the cost of the fluctuating signal.

The TDPAC measurements have been performed at different lower temperatures after the sample was

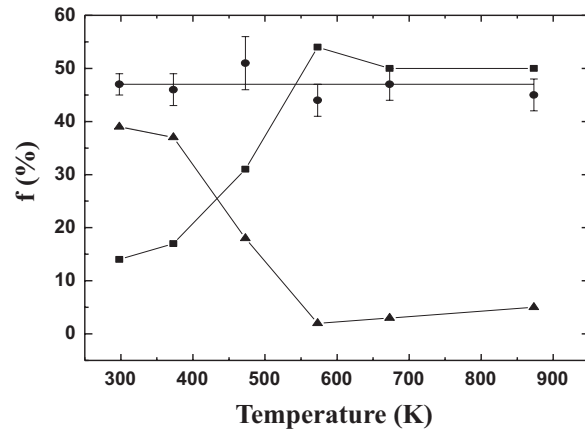


Fig. 4. Variations of component fractions with temperature corresponding to monoclinic HfO_2 (●), fluctuating (■) hcp Hf, and total static defect hcp Hf components (▲).

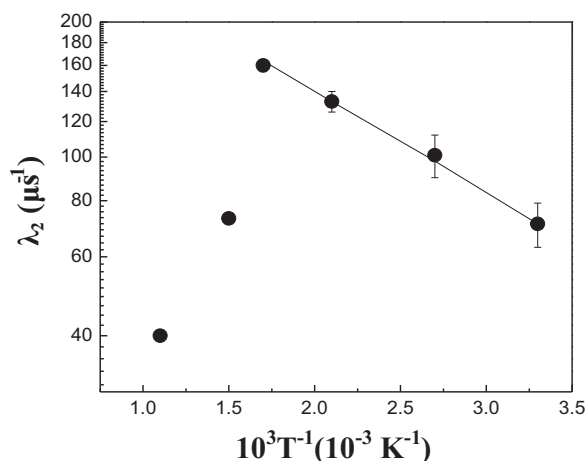


Fig. 5. Dependence of the relaxation constant λ_2 with inverse temperature ($1/T$) after the sample was heated at 873 K for two days in air.

heated for two days at 873 K. The results are shown in Figure 3. At 673 K, the static frequency component due to HfO_2 does not change and the fluctuating strength is found to be same as found at 873 K. At 573 K also, the relative component fractions due to static HfO_2 and time-dependent interaction do not change appreciably. But at 473 K, the static frequency component due to HfO_2 while remaining same (47%), the fluctuating component decreases to 31% (Fig. 4). At this temperature, apart from the main static HfO_2 component, two other minor components (9% each) are observed (Tab. 2). These minor components can be attributed to two defect configurations of hcp Hf since the quadrupole frequencies for these minor components are very much closer to the hcp Hf frequency. At 373 K, the fluctuating signal is further reduced to $\sim 17\%$ and the total hcp defect components enhances to $\sim 37\%$ while the HfO_2 component remains same. When the measurement was performed at room temperature, the fluctuating signal is still found to be present ($\sim 14\%$). At this temperature, two defect fractions of Hf appear (Tab. 2) with relatively higher percentages.

The relaxation constants at different temperature also change with temperature. At 773 K, the value of relaxation constant is increased to a value of $74/\mu\text{s}$. In fact, it is found that the relaxation constants increase strongly with lowering of temperature up to 573 K where a maximum value of $\lambda_2 = 160/\mu\text{s}$ is found (Fig. 5). After that, the value of λ_2 decreases slowly

with reduction of temperature while the fluctuating strength decreases strongly in the temperature regime 473–298 K. Thus, the fluctuation of Hf atoms in the temperature regime 873–573 K can be described as fast-fluctuation regime and at temperatures lower than 573 K this fluctuation can be described as in the slow-fluctuation regime.

In the slow-fluctuation regime (Fig. 5, right side), an exponential fitting (3) of the relaxation constants found at different temperatures gives the value of activation energy $E_A = 0.04(1)$ eV. The activation energy gives the potential energy barrier that an Hf atom encounters when it jumps from an occupied site to a vacant site in the lattice by thermal energy. The quadrupole frequency corresponding to a fluctuating electric field gradient can be determined using the relation $\lambda_2^{\text{max}} (\mu\text{s}^{-1}) \approx 3\omega_Q^f \text{ Mrad/s}$ [18]. This has been found to be $\approx 53 \text{ Mrad/s}$ for the value of $\lambda_2^{\text{max}} = 160 \mu\text{s}^{-1}$ found at a temperature of 573 K. This value of ω_Q^f matches well with the value of the quadrupole frequency of hcp Hf ($\sim 50 \text{ Mrad/s}$) and supports again that spin relaxations observed at 873 K and lower temperatures are due to fluctuations of Hf atoms.

In the fast-fluctuation regime (Fig. 5, left side), the relaxation constants change rapidly with temperature and there are three data points which are not perfectly on the same line. However, a value of $E_A \sim 0.07(2)$ eV has been estimated in this regime from the data points at 873 and 673 K (two extreme points in the fast fluctuation regime). This shows that activation energies of Hf atoms in the fast and slow-fluctuation regimes are closer to each other.

4. Conclusion

The microscopic behaviours of Hf metal with temperature are found to be interesting which are not observed previously. From time-differential perturbed angular correlation (TDPAC) measurements it has been clearly demonstrated that the oxide formation of this metal does not follow the Arrhenius behaviour with temperature when heated in air. From the Arrhenius theory, the growth rate of oxide ($\ln f$) is expected to vary linearly with temperature T . From present measurements, it is found that HfO_2 grows abruptly at 873 K when Hf metal is heated in air continuously for two days while there was no oxide formation up to 773 K or in the initial heating at 873 K for one day. The fluctuation of Hf atoms at 873 K is a new infor-

mation obtained from present measurements. In the heating of Hf metal at 873 K continuously for two days in air, Hf atoms in the hcp Hf crystal produce a complete fluctuating behaviour where no static frequency component due to this crystalline structure is observed. The static components appear as different defect configurations of Hf when the temperature is gradually reduced. Observation of the complete fluctuating behaviour of Hf atoms in the hcp Hf is definitely an interesting result when the melting point of Hf is much above 873 K. Thus, at a temperature much lower than its melting point a state of completely fluctuating behaviour of atoms is produced in a metal on

prolong heating where no crystalline structure is observed.

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