Self-diffusion processes in stoichiometric iron mononitride

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In this work, we studied atomic self-diffusion and structural phase transformation in a single phase iron mononitride (FeN) thin film deposited at an optimized substrate temperature (T_s) of 423 K. At this T_s , FeN film exhibit a tetrahedral coordination between Fe and N atoms (ZnS-type structure with lattice parameter of 4.28 Å). The structure of FeN film was studied by combining x-ray diffraction with Fe and N K-edge x-ray absorption spectroscopy and conversion electron Mössbauer spectroscopy measurements. Self-diffusion of Fe and N was measured using secondary ion mass spectroscopy depth profiling in trilayer structures: [FeN(50 nm)/⁵⁷FeN(2 nm)/FeN(50 nm)] and [FeN(50 nm)/Fe¹⁵N(2 nm)/FeN(50 nm)] deposited on an amorphous quartz substrate using reactive magnetron sputtering. It was found that atomic self-diffusion is strongly associated with the thermal stability. Before reaching the phase decomposition temperature, the self-diffusion of N was found to be slower than Fe. Upon phase decomposition, both Fe and N diffuse rapidly, and at this stage, the self-diffusion of N takes over Fe. Within the thermally stable state, slower N diffusion indicates that Fe-N bonds are stronger than Fe-Fe bonds in FeN. This behavior was predicted theoretically and has been evidenced in this work.

I. INTRODUCTION

3d transition metal nitrides (TMN) specially those appearing late in the series (e.g. Fe-N, Co-N, Ni-N), are relatively less explored materials as compared to their oxides.¹ Since the bond enthalpy of a triply bonded N₂ molecule at 946 kJ mol⁻¹ is about twice that of O₂, formation of TM oxides is comparatively easier.² However, in a plasma based synthesis method, typically that are found in physical vapor deposition, increased ratio of nitrogen ions may assist the formation of some phases that do not exist in the bulk. Iron mononitride (FeN) is one such compound, which has been deposited frequently using reactive magnetron sputtering³⁻¹⁰ and recently using nitrogen plasma assisted molecular beam epitaxy.¹¹ Theoretical studies suggest that the enthalpy of formation (ΔH_f°) for FeN¹² is about -45 kJ mol⁻¹ which is considerably higher (less negative) than that of early TM mononitrides e.g. $\Delta H_f^\circ = -338$ kJ mol⁻¹ for TiN.^{13,14} Under such energetically unfavorable conditions, it can be anticipated that FeN would be less stable as compared to early TMNs as well as other Fe-rich nitrides which are known for their corrosion resistance properties and used as superhard coatings.¹⁵⁻²⁰ Apart from fundamental interests, FeN has been portrayed as a material of choice in various magnetic^{21,22} as well as energy storage and conversion devices.^{23,24}

Among 3d binary nitrides, a clear distinction between the early and the late TMNs can be seen. While all early TMNs e.g. VN, TiN, CrN etc. have a common

fcc rock salt (RS) type structure - FeN and CoN have been claimed to have a mixture of RS and/or zinc-blende (ZB) type structures. Recent theoretical works on FeN predict a number of structures other than ZB and RS namely, NiAs type, CsCl type and MnP type.^{25,26} Experimentally, FeN has only been synthesized in ZB and RS structure under ambient conditions^{4,8-10,27,28}, however, the existence of RS structure is still a matter of debate^{29,30} while NiAs type structure has recently been evidenced at high-temperature and high-pressure conditions.³¹⁻³³ Meanwhile, a structural transition has been predicted from ZB structure to RS and NiAs at high pressure (> 50 GPa).²⁵ With increase in pressure above 100 GPa and temperature above 2000 K, N-rich phases such as FeN₂, FeN₄ have also been obtained recently and these phases consist of polymeric chain of singly bonded N atoms which makes them potential candidates in high energy density materials.^{34,35}

In addition, issues related with the thermal instability of FeN can be best addressed by measuring atomic diffusion in these systems. In recent works, a rather surprising result was found for Fe and N self-diffusion; Fe self-diffusion was found to be faster than N.^{6,27,28} It was suggested that the involved diffusion processes for Fe and N atoms are different. While N atoms follow a conventional volume type diffusion process, Fe diffusion predominantly takes place through grain boundaries (gb).⁶ In order to investigate this behavior further, in the present work, we report a detailed study on the structure and self-diffusion behavior in FeN. By optimizing the substrate temperature (T_s) to 423 K, we could synthesize a single phase and stoichiometric FeN film using a reactive magnetron sputtering process.³⁰ Structural measurements performed using x-ray diffraction (XRD) and x-ray

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absorption near edge spectroscopy (XANES) at Fe and N K-edges indicate the formation of a crystalline FeN compound with the ZB type structure. Our low temperature Mössbauer spectroscopy (MS) measurements confirm the non-magnetic ground state expected in ZB-FeN while conversion electron Mössbauer spectroscopy (CEMS) indicates that the defect fraction in ZB type FeN reduces significantly when deposited at an optimized T_s of 423 K. At a T_s of 423 K, it is expected that the volume fraction of gb will be smaller and therefore, gb diffusion is expected to be negligible as compared to samples deposited at $T_s = 300$ K (no heating). This was indeed found from Fe and N self-diffusion measurements carried out using secondary ion mass spectroscopy (SIMS) in this work. However, at lower temperatures (between 423 K to 525 K), we found that Fe self-diffusion is still somewhat faster than that of N, and can be explained in terms of Fe-Fe and Fe-N bond distances in FeN. Since we found that the distance between metal-metal and metal-nitrogen atoms plays a pivotal role in affecting the atomic self-diffusion in metal nitrides, obtained results can be extended to other members of TMN family.

II. EXPERIMENTAL PROCEDURE

We deposited samples on quartz (SiO_2) substrate by placing an isotopic enriched layer of ^{57}FeN or Fe^{15}N between their naturally occurring counterparts labelled as:
A: [$\text{FeN}(50\text{ nm})/^{57}\text{FeN}(2\text{ nm})/\text{FeN}(50\text{ nm})$]
B: [$\text{FeN}(50\text{ nm})/\text{Fe}^{15}\text{N}(2\text{ nm})/\text{FeN}(50\text{ nm})$]

A direct current magnetron sputtering (dcMS) system was used at a constant power of 100 W. Samples were deposited using nitrogen (99.9995% purity) alone as sputtering medium at $T_s = 423$ K. After attaining a base pressure of about 5×10^{-8} mbar, N_2 gas was flown into the chamber at a flow rate of 50 sccm and the pressure during deposition was 2.5×10^{-3} mbar. For sample *A*, a Fe (99.995%) $\phi 3$ -inch, 1 mm thick and a ^{57}Fe (95% enriched) $\phi 1$ -inch, 0.4 mm thick targets were used. For sample *B*, the $\phi 3$ -inch Fe target was sputtered alternatively with natural N_2 and $^{15}\text{N}_2$ (98% enriched) gases. A residual gas analyzer was installed in the sputtering system to monitor the presence of natural N_2 and $^{15}\text{N}_2$ gases.

Samples were characterized for their structure using a standard powder XRD system equipped with Cu $k\alpha$ source and a 1D position sensitive detector (Bruker LynxEye). The local structure of the samples was investigated using conversion electron Mössbauer spectroscopy (CEMS) and x-ray absorption near edge spectroscopy (XANES) measurements at N and Fe K-edge. N K-edge XANES was performed at BL-01 of INDUS-2 synchrotron facility at RRCAT, Indore³⁶ while Fe K-edge XANES was measured at P64 beamline at DESY Hamburg, Germany.³⁷ N K-edge was measured in the total electron yield (TEY) mode while Fe K-edge was measured in fluorescence geometry. Since TEY mode is surface sensitive, samples were sputtered to remove about

20 nm of top layer using a 5 KeV, $50\mu\text{A}$ Ar^+ source incident at an angle of 45° . Comparing the sputtered and in-situ grown N K-edge spectra³⁸, it can be anticipated that sputtering of FeN sample does not severally affect the integrity of atomic arrangement in FeN sample. Local magnetic structure of samples was investigated using Mössbauer spectroscopy (MS) carried out at 300 K and also at low temperature (100 K) using a liquid He cryomagnet. In this case gamma rays were allowed to pass through a thin Si substrate and measurements were done in transmission geometry.

Self-diffusion measurements in samples *A* and *B* were carried out using secondary ion mass spectroscopy (SIMS). A Hiden SIMS workstation was used with oxygen ions as a primary ion source operating at 5 KeV and 400 nA. With a base pressure of 5×10^{-10} mbar, the pressure with differentially pumped ion source operating was about 5×10^{-8} mbar. Secondary ions were detected using a quadrupole mass analyzer. The thermal annealing of the samples was carried out in a vacuum furnace with a base pressure of 1×10^{-7} mbar and at each annealing temperature, samples were annealed for 1 h.

III. RESULTS AND DISCUSSION

As mentioned already, single phase and stoichiometric FeN thin film samples with a preferred orientation along (111) direction were grown at an optimized $T_s = 423$ K.³⁰ Their thermal stability was obtained by doing XRD and CEMS measurements on isochronally (1 h) annealed samples at different temperatures. Fig. 1(a) compares XRD patterns of the as-deposited sample with those annealed at 473, 523, 573 and 623 K. The structure of as-deposited sample can be identified as ZB-type FeN with LP = 4.28 Å. This value is close to the experimental value obtained in various works but somewhat higher than the theoretically predicted value of about 4.23 Å.^{10,11,20,25} As shown in our recent work, the T_s of 423 K was found to be the optimum to attain a stoichiometric FeN phase with the LP closest to its theoretical value. When FeN film was deposited at $T_s = 300$ K (without any intentional substrate heating), the LP comes out to be 4.5 Å, which is much higher than the theoretically predicted value. This happens due to an intrinsic compressive stress present in the film due to adatom trapping at the grain boundaries.³⁰

Moreover, the film deposited at 300 K also consists of a nanocrystalline structure with high number of grain boundaries as the crystallite size was found to be ≈ 5 nm.^{30,39} However, when FeN is deposited at an optimized T_s of 423 K, the crystallite size estimated from the width of (111) peak comes out to be much larger at about 18 nm. This suggests a reduced number of grain boundaries as expected at a high T_s . It can be further seen from fig. 1(a) that the thermal annealing up to 523 K does not affect the XRD pattern and the crystallite size also remains similar after annealing it to 473 and 523 K. There-

fore, no structural relaxation was observed with thermal annealing upto 523 K which again infers that free volume associated with the grain boundaries gets reduced when FeN is deposited at a high T_s of 423 K. However, annealing at 573 K results in the appearance of peaks corresponding to Fe_{3-y}N ($0 \leq y < 1$) and they become even stronger after annealing at 623 K.

A similar behavior can also be seen from the CEMS spectra shown in fig. 1(b) and they were fitted using NORMOS/SITE program.⁴⁰ The CEMS spectrum of the as-deposited sample resembles a single line shape that has some asymmetry at the onset. It was fitted by deconvoluting into two singlets namely, S1 and S2. The magnitude of isomer shift (relative to $\alpha\text{-Fe}$) for the singlet S1 was about 0.07 mm/s but for the component S2, it was much larger at about 0.32 mm/s. In FeN, the component S1 with isomer shift near to 0 mm/s corresponds to Fe tetrahedrally coordinated with four N atoms, while the component S2 originates due to some vacancies of N atom at the nearest neighbor Fe site.^{4,41} From the fitting of CEMS data, we find that the fraction of S1 and S2 comes out to be 0.75 and 0.25, respectively and matching well with ZB-FeN.²⁹ Similar to the results obtained from XRD measurements, we find that annealing of the sample up to a temperature of 523 K does not result in any significant change in the CEMS spectrum and the fitting parameters also remain almost identical to the as-deposited sample. Therefore, measurement of the long-range crystalline ordering from XRD and the local structure from CEMS confirm that FeN remains thermally stable up to 523 K. The CEMS pattern of the sample annealed above this temperature confirm the decomposition of FeN into Fe_{3-y}N phase. From the fitting of CEMS data of sample annealed at 623 K the estimated hyperfine field comes out to be about 22 T in agreement with the previous reports.^{10,39}

We also investigated the local magnetic structure of as-deposited FeN sample by performing Mössbauer spectroscopy measurements at 300 and 100 K in the transmission mode (incident gamma rays pass through the sample on a Si substrate) as shown in the inset of fig. 1(b). Since, in this mode, a considerable amount of signal is absorbed, a sample with about 50 nm thick ^{57}Fe film was prepared under identical conditions. We find that the spectrum taken at 300 K is essentially a single line and it remains similar when the sample temperature is reduced to 100 K. Since we measured Mössbauer spectra at a higher velocity to verify the presence of any magnetic ordering, detailed fitting of Mössbauer spectra has already been discussed in the case of CEMS measurements shown in fig. 1(b). Absence of any magnetic ordering in MS patterns further confirm that the sample remains non-magnetic down to 100 K.

We then studied the local structure of the as-deposited FeN sample using Fe and N K-edge XANES spectra as shown in fig. 1(c) and (d), respectively. In N K-edge, we find features labeled as *a*, *b*, *c*, *d* and *e*. Since the N K-edge in FeN is not well-established yet,^{30,39} it can be

compared with TiN in which N K-edge XANES is well studied.^{42,43} Features *a* and *b* in TiN correspond to electronic transition from $\text{N}1s$ to the unoccupied hybridized state of $\text{Ti}3d$ and $\text{N}2p$ states and features at higher energies (*c-e*) arise due to transition from $\text{N}1s$ to hybridized $\text{N}2p$ states with $\text{Ti}4sp$ states. These features are comparable in N K-edge of FeN, however, changes in the intensity of features *a* and *b* can be seen which is attributed to the tetrahedral symmetry present in the ZB structure of FeN while TiN possess octahedral symmetry in RS structure. Therefore, features *a* and *b* corresponds to t_{2g} and e_g orbitals in TiN which are completely unoccupied while in case of FeN, these features denote partially filled *e* and t_2 orbitals. Moreover, Fe K-edge consists of a strong pre-edge peak at 7114 eV which is a characteristic feature of tetrahedral symmetry present in ZB type FeN and the main absorption edge originates at 7129 eV due to dipole transition of $1s$ core electron of Fe into $4p$ conduction band. Such an intense pre-edge feature also indicates the more ordered structure of FeN as the intensity of pre-edge depends on the local coordination around Fe atoms which varies with the application of T_s .³⁰ Therefore, our XRD and XANES spectra indicate that FeN films deposited at 423 K are well crystalline and have ZB type structure in which N is tetrahedrally bonded with Fe while MS measurements confirms the non-magnetic ground state for ZB-FeN.

The long-range crystalline ordering in FeN phase could also affect the diffusion processes. Since, the nanocrystalline films with an average grain size of about 5 nm consists of a large number of grain boundaries which may lead to high density of defects in the FeN system. Such defects in FeN have been quantified using CEMS measurements. It is clear that with the optimization of T_s , the fraction of defects reduces significantly as the S2 phase fraction in the present case is about 25%, while it was as high as 50% when FeN was deposited at 300 K.²⁸ It is known that the diffusion process strictly depends on the amount of defects in the thin films. Therefore, the formation of N poor phase upon thermal annealing of FeN can be correlated with Fe and N diffusion in FeN. In a work by Tayal et al., such diffusion process was studied in nanocrystalline FeN thin film and a dominant grain boundary (gb) diffusion was observed for Fe atoms below 525 K.³⁹ However, it is proposed that the gb diffusion can be controlled by reducing gb defects in the various metallic as well as metal-metalloid systems.⁴⁴⁻⁴⁶ Therefore, in order to understand the role of defects on the self-diffusion of Fe and N, we performed SIMS depth profiling measurements on samples *A* and *B*, respectively, both below and above phase decomposition temperature.

Fig. 2(a) and (b) shows ^{15}N and ^{57}Fe SIMS depth profiles respectively, in the as-deposited state and after annealing the samples at different temperatures for 1 h at each temperature. As can be seen from fig. 2, the width of ^{57}Fe profile is significantly larger than that of ^{15}N . This essentially happens because of faster Fe diffusion taking place through gb during the deposition itself.⁴⁷

FIG. 1. (a) x-ray diffraction (b) conversion electron Mössbauer spectroscopy (CEMS) patterns for iron mononitride (FeN) thin films deposited at a substrate temperature, $T_s = 423$ K and then annealed at various temperatures. Inset in (b) shows MS patterns for as-deposited ^{57}Fe thin film measured at 300 and 100 K (c) Fe and (d) N K-edge XANES patterns of as-deposited FeN thin film where N K-edge was also compared with that of TiN.

FIG. 2. SIMS depth profile of FeN/ ^{57}Fe N/FeN (a) and that of FeN/Fe ^{15}N /FeN (b) samples deposited at $T_s = 423$ K in the as-deposited state and after annealing at different temperatures.

With an increase in annealing temperature up to 523 K, the widths of the profiles increases marginally due to reduced Fe and N diffusion. However, at 548 K, peak corresponding to ^{15}N almost disappears indicating a rapid increase in N diffusion while changes in Fe diffusion are not as subtle.

By applying the thin film solution to Fick's law, we can write the tracer concentration $c(x, t)$ of ^{15}N and ^{57}Fe as a function of penetration depth (x) using the equation^{48,49}

$$c(x, t) = \frac{c'}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (1)$$

FIG. 3. Arrhenius behavior of Fe and N self-diffusion and correlation between self-diffusion and phase transformation in FeN thin film.

where c' is a constant, D is diffusion coefficient and t is the annealing time. Therefore, both ^{57}Fe and ^{15}N depth profiles were fitted using a gaussian distribution function and the corresponding diffusion coefficients were calculated using the following equation:

$$D(t) = \frac{\sigma_t^2 - \sigma_0^2}{2t}, \quad (2)$$

where σ_0 is the standard deviation of gaussian depth profile before annealing i.e. at $t=0$ and σ_t is the standard deviation after annealing time, t .

Obtained Fe and N diffusivities are then plotted in fig. 3. Below the phase decomposition temperature (523 K), the behavior of Fe and N diffusivity is similar; however, absolute values of N diffusion are still lower than

FIG. 4. Correlation between $\ln D_0$ and E_a for multilayers, crystalline and amorphous alloys taken from literature⁵⁰. Here solid triangle ($\blacktriangle$) and star ($\star$) represents the Fe and N diffusivity obtained in this work for samples A and B, respectively.

Fe. This may be due to some gb diffusion which is not yet completed. But since SIMS depth profiles of ^{57}Fe can be fitted using a gaussian distribution alone, it can be anticipated that Fe atoms are pre-dominantly diffusing through a volume type diffusion process similar to N atoms. Obtained values of diffusivity can be fitted using an Arrhenius equation given by $D = D_0 \exp(-E_a/k_B T)$, where D_0 is the pre-exponential factor, E_a is activation energy, T is annealing temperature and k_B is Boltzmann's constant. From fig. 3, it can be seen that below 523 K, the E_a values obtained for Fe (0.43 ± 0.06 eV) and N (0.35 ± 0.07 eV) self-diffusion are almost similar while D_0 is about an order of magnitude smaller for N (1.2×10^{-18} m²/s) than for Fe (1.5×10^{-17} m²/s). As the annealing temperature increases, N diffusion increases rapidly. At 548 K, ^{15}N profile vanishes almost completely but ^{57}Fe profile shows relatively smaller changes. The value of diffusivity at 548 K is two orders of magnitude larger for N than Fe as shown in fig. 3. Across the phase decomposition (between 523 and 573 K), we find $E_a = 1.6(0.2)$ eV and $D_0 = 6.0 \times 10^{-6}$ m²/s for Fe self-diffusion while N self-diffusion coefficient at this stage becomes too fast to measure experimentally.

It may be noted that D_0 and E_a are also termed as activation parameters⁵¹ and their experimental values follows a isokinetic correlation given by^{50,52}

$$\ln D_0 = \ln X + \frac{E_a}{Y} \quad (3)$$

where X and Y are constants. This correlation exhibits a universal character and followed by a vast range of materials including amorphous as well as crystalline alloys. Therefore, we compared our experimental values of activation parameters (D_0 , E_a) for Fe and N self-diffusion before phase decomposition, with the available literature as shown in fig. 4. We observed that the values in the present case are in well accordance with the literature and the activation parameters for nanocrystalline FeN samples are correlated with interdiffusion in multilayers with the values of X and Y as 7×10^{-23} m²/s and 0.047 eV, respectively. The correlation defined in eq. 3 reveals the

mechanism associated with the diffusion process for a particular set of values of constants X and Y .^{50,53} As per Zener's theory of pre-exponential factor, we can also define D_0 as follows⁴⁸

$$\ln D_0 = \ln g a^2 f \nu_0 + \frac{\Delta S}{k_B} \quad (4)$$

Here, g is geometric factor, a is the atomic jump distance, f is the correlation factor, ν_0 is the effective jump attempt frequency, and ΔS is the change in activation entropy during jump process. The large differences in the values of D_0 for a range of materials from multilayers to amorphous and crystalline alloys originates from the entropy term only as other factors do not vary much among the materials. Therefore, by using the eq. 3 and eq. 4, we can calculate change in entropy, ΔS which accounts for the number of atoms participating in the diffusion process. For Fe and N self-diffusion, the values of ΔS are $9(1)k_B$ and $7(1)k_B$, respectively, which are quite similar and lies in the range of multilayers (8 to $15k_B$).⁵³ The almost equal values of ΔS denotes that Fe and N self-diffusion involves a similar yet smaller group of atoms which is usually the case of defect mediated diffusion processes such as vacancy type, interstitial and/or gb defects. Although FeN is N-rich phase with most of the interstitial sites occupied by N atoms, the probability of few vacant interstitial sites would still be possible as observed from our CEMS measurements. Therefore, N self-diffusion involves interstitial mechanism while Fe being the host matrix would diffuse via vacancy and/or gb defects. However, in present case, we already observed that the gb diffusion is not a dominant process for Fe self-diffusion when FeN is deposited at an optimized T_s of 423 K. Hence, Fe atoms must diffuse via vacancy mechanism which is a slower process as compared to gb diffusion.³⁹

Combining the above results, we observed that below the phase decomposition temperature (523 K), Fe diffusion dominates over N, while above it, the diffusion of N becomes faster than Fe. Such anomalous behavior of Fe in spite of being a larger atom, its faster than N diffusion can be understood in terms of a stronger interaction between Fe-N as compared to that of Fe-Fe interactions. For late 3d TMN, the theoretical calculations predicted a rearrangement of electron density between metal-metal and metal-nitrogen bonds. A comparison of bond distances in Fe and FeN has been shown in fig. 5. Also, the expansion in metal lattice in order to occupy N atoms at the interstitial sites weakens the metal-metal bonding and due to shift in electron density from metal-metal to metal-nitrogen bond, the latter ones gets strengthened.⁵⁴ This makes it easier to break the Fe-Fe bonds than Fe-N bonds leading to faster Fe diffusion. In addition, FeN thin film also consists of intrinsic defects which also accelerates the diffusion processes.

Hence, the results obtained in this study clearly suggest that the phase decomposition in FeN is deeply associated with the atomic diffusion which also depends on

FIG. 5. Structure of bcc Fe and ZB-FeN. Here, blue sphere denotes Fe and green sphere denotes interstitial N atoms. The bond distances in FeN are taken from³⁰.

the amount of the defects present in the system. By optimizing the T_s , we are able to enhance the long-range crystalline ordering in FeN which also results in reducing the gb defects but we could not prevent the phase decomposition of FeN into N poor phases. However, unlike the case of nanocrystalline FeN, we only observed vacancy type diffusion for Fe atoms in present case. Therefore, further optimization of process parameters would not help much in controlling the Fe self-diffusion. Since, it is Fe which is diffusing faster (than N) below phase decomposition temperature (523 K), one can utilize some suitable dopant to further control the Fe self-diffusion in FeN.

CONCLUSIONS

In this work, we studied the role of Fe and N self-diffusion on structural phase transformation in a single phase and stoichiometric iron mononitride thin film. This sample was deposited at an optimized substrate temperature of 423 K and it was found that FeN is thermally stable upto 523 K. Beyond it, FeN decomposes into N poor phases (Fe_{3-y}N ($0 \leq y < 1$)) owing to Fe and N self-diffusion. From SIMS measurements, it was observed that in the thermally stable regime, diffusivity of Fe is about a order of magnitude higher than N indicating faster Fe self-diffusion while after phase decomposition, N diffusion dominates over Fe. The CEMS results for the as-deposited sample indicates that the defects in FeN compound decreases significantly after optimizing the T_s and hence, we are able to suppress the dominant grain boundary diffusion of Fe in FeN.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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