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Role of sputtered atom and ion energy distribution in films deposited by physical vapor deposition: A molecular dynamics approach

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ABSTRACT

We present a comparative molecular dynamics simulation study of copper film growth between various physical vapor deposition (PVD) techniques: a constant energy neutral beam, thermal evaporation, dc magnetron sputtering, high-power impulse magnetron sputtering (HiPIMS), and bipolar HiPIMS. Experimentally determined energy distribution functions were utilized to model the deposition processes. Our results indicate significant differences in the film quality, growth rate, and substrate erosion. Bipolar HiPIMS shows the potential for an improved film structure under certain conditions, albeit with increased substrate erosion. Bipolar HiPIMS (+180 V and 10% Cu⁺ ions) exhibited the best film properties in terms of crystallinity and atomic stress among the PVD processes investigated.

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I. INTRODUCTION

Molecular dynamics (MD) simulation is a simulation technique well suited for describing thin film or nanoparticle growth phenomena.^{1–4} Here, MD simulations are applied to compare the growth of thin copper (Cu) films using various physical vapor deposition (PVD) techniques.⁵ The deposition systems assumed in the present work include a constant energy neutral beam, thermal evaporation, dc magnetron sputtering (dcMS), high-power impulse magnetron sputtering (HiPIMS), and bipolar HiPIMS.^{5,6} In neutral beam, thermal evaporation, and dcMS depositions, the film forming species are neutral atoms. In HiPIMS operation, the magnetron sputtering discharge is driven by high-power pulses at low frequency and a short duty cycle,^{6,7} and the ionized flux fraction of the sputtered species can be high,⁸ and furthermore, the ion energy can be significantly higher than in dcMS operation.⁹ In bipolar

HiPIMS operation, a positive voltage is applied to the target following the negative sputter pulse, which increases the plasma potential and shifts the ion energy distribution (IED) to higher energies.^{10–13} Some successful attempts have been made to include the specific characteristics of different magnetron sputtering (MS) deposition techniques into MD simulations, the role of the ionized flux fraction,¹⁴ the ion potential energy,¹⁵ and the IED shift due to substrate bias,¹⁶ which show varying film properties depending on the deposition method. Usually, in MD simulations, this is achieved by setting mean kinetic energy or sampling from a uniform energy distribution. The earlier studies were based on a uniform IED, while in practice, the IED is meant to demonstrate that the probability of certain energies can vary depending on the deposition method. Here, we further improve the description of the physically released film forming species by using selected initial velocity

conditions from experimental data (energy-resolved mass spectrometry) and SRIM simulations¹⁷ for the IED and the atom energy distribution (AED). This choice was motivated by approximating the experimental conditions as closely as possible. Further improvement of the initial conditions is expected to give a step forward for a more realistic MD simulation and, thus, a more accurate prediction of sputtered film properties, such as morphology, composition, structure, and tribology.

II. EXPERIMENTAL SETUP AND RESULTS

The reactor used to determine the IED for the magnetron sputtering processes is made up of a central chamber, which is a cylindrical stainless-steel enclosure with a diameter of 200 mm. It contained six crossed flanges with an external diameter of 240 mm (ISO-K200). The first flange was connected to a pumping system that ensured a vacuum of approximately 5×10^{-5} Pa using a primary pump (Pfeiffer vacuum, ACP15, 15 m³/h) and a turbo-molecular pump (Pfeiffer vacuum, 500 l/s). The lamination valve placed between the chamber and the turbo-molecular pump made it possible to adjust the working gas pressure inside the enclosure, and the two gauges (a combined Pirani/cold cathode gauge and a baratron gauge) made it possible to measure this pressure. The magnetron assembly [Angstrom Sciences (ONYX-2)] where the sputtering target (copper) is placed had a diameter of 2 in. It was placed facing the EQP1000 300 amu Hiden Analytical mass spectrometer at a distance of 10 cm. A pulsed power module (Starfire Industries), which contains a solid-state switching device, was fed by a Kurt J. Lesker PDX 500 DC generator. This system can be used to power the magnetron sputtering discharge with unipolar pulses (HiPIMS) or bipolar pulses (bipolar HiPIMS) with a voltage limit of 1000 V. The current-voltage characteristics were observed using a Tektronix oscilloscope. Argon was used as the working gas, set at 0.7 Pa, and the flow rate was regulated at 40 sccm using a Bronkhorst mass flow meter (F-200CV). In the present work, the HiPIMS sputter pulse was 50 μ s long and the negative bias -650 V. In a bipolar HiPIMS configuration, the negative pulse was followed by a longer pulse (250 μ s) with a positive bias varying from +20 to +180 V. Figure 1 shows the corresponding experimentally recorded IEDs for Cu⁺ ions measured 10 cm from the Cu target center.

III. MOLECULAR DYNAMICS SIMULATION SETUP

Molecular dynamics simulations allow the calculation of the trajectories of a set of species by solving Newton's equations of motion,

$$m_i \frac{d^2 \vec{r}_i(t)}{dt^2} = \vec{F}_i = -\vec{\nabla} V(\vec{r}_1(t), \vec{r}_2(t), \dots, \vec{r}_N(t)), \quad (1)$$

where $\vec{r}_i(t)$ is the position of atom i at time t with mass m_i , and V is the interaction potential between all N involved species. These equations only require knowledge of two initial conditions, positions, and velocities for all species at the initial time $t = 0$, and of the interactions between all species at all times. The initial positions refer to the geometry/topology of the particles at the beginning of the simulation, while velocities are (randomly) selected from a velocity distribution that is consistent with the deposition method

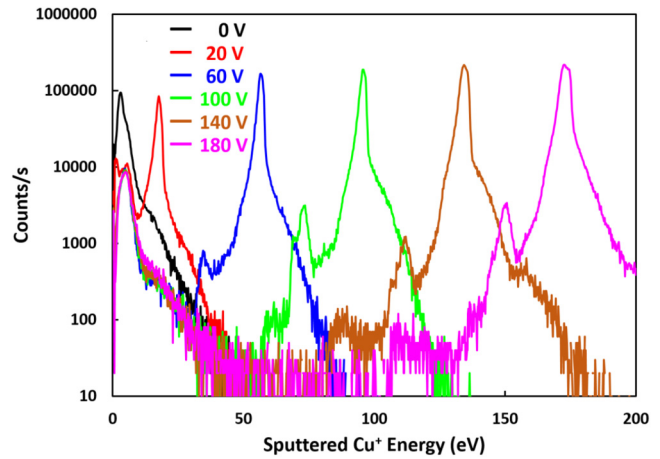


FIG. 1. Experimentally determined copper Cu⁺ ion energy distributions (IEDs) (semilog scale) in an HiPIMS mode (0 V) and bipolar HiPIMS for various positive voltages recorded 10 cm away from the target surface.

under study. To examine the effect of the AEDs and IEDs on the deposited films, we considered an AISI 3016L stainless-steel substrate (bcc Fe₆₇Cr₁₇Mo₂Ni₁₄, $72 \times 72 \times 46 \text{ \AA}^3$ slab composed of 20 000 atoms). The stainless-steel substrate is composed of fixed layers, Langevin thermostated layers, and layers free to move as seen in Fig. 2, showing the initial simulation box. For a constant energy neutral beam, thermal evaporation, and dcMS, 10 000 neutral Cu atoms are periodically released toward the surface. In the case of HiPIMS and bipolar HiPIMS, 10 000 species composed of 90% Cu + 10% Cu⁺ or 50% Cu + 50% Cu⁺ were released at a periodic rate from random positions above the surface. Such neutral and ion compositions are chosen for mimicking low and high ion flux toward the substrate. Sets of 10 Cu (or $x\text{Cu} + y\text{Cu}^+$) atoms, randomly located above the surface and sufficiently far from

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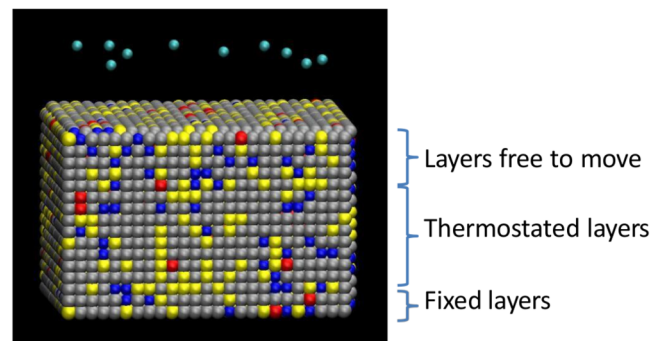


FIG. 2. Simulation box with the stainless-steel substrate and the first set of ten atoms/ions before release toward the surface. A Langevin thermostat is used for the thermostated layers. Color code: cyan Cu, yellow Cr, silver Fe, red Mo, and blue Ni.

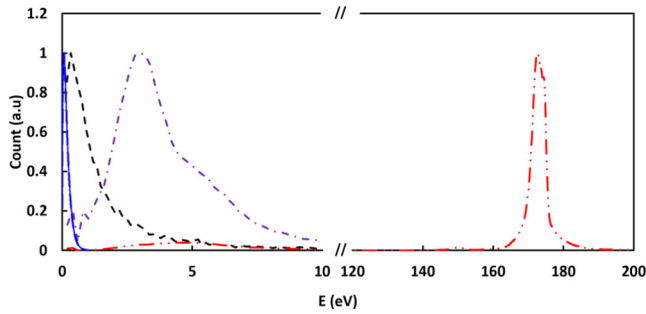


FIG. 3. Sputtered Cu atom and ion energy distributions (linear scale). — blue: Thermal evaporation at 1358 K (AED), - - - black: dcMS SRIM propagated along a 10 cm target to a substrate path, at 0.7 Pa (AED), - · - · purple: HiPIMS Cu⁺, Exp QMS at 10 cm and 0.7 Pa (IED), · · · · red: bipolar HiPIMS (+180 V) (IED).

each other, were released every 40 ps. Thus, the total simulation time was 40 ns.

The initial velocities are randomly selected from the corresponding AEDs and IEDs. For thermal evaporation, a Maxwell-Boltzmann distribution at a melting temperature is considered; for dcMS, SRIM AED modified by transport through the MS reactor is used.¹ For HiPIMS and bipolar HiPIMS, the kinetic energy of the

sputtered ions was selected from the experimental energy-resolved mass spectra (Fig. 3), while that of sputtered neutral Cu was assumed similar to dcMS and were selected in the corresponding AED. The constant kinetic beamlike Cu energy was chosen as the mean kinetic energy of the SRIM AED propagated through 10 cm at 0.7 Pa. Figure 3 shows the different AEDs and IEDs used in this study. The embedded atom method was chosen to describe Cu, Fe, Cr, Ni, and Mo interactions.^{18,19} Cross interactions use the Johnson mixing rule.²⁰

IV. SIMULATION RESULTS

Figure 4 shows the resulting deposited films with different initial conditions, mimicking the different deposition processes, while Table I summarizes the properties of the simulated films. The more aggressive deposition condition, bipolar HiPIMS (+180 V 50% Cu –50% Cu⁺), results in high interface mixing and a low Cu content, suggesting Cu⁺ sputtering of the depositing film since the acceleration voltage was 180 V. This was not visible in the 10% Cu⁺ conditions owing to the lower Cu⁺ ion flux. The atomic structures of the films were calculated using the polyhedral template matching method²¹ available in the OVITO software.²² The highest structural film quality (60% fcc) was achieved by the monoenergetic neutral beam with the kinetic energy corresponding to the dcMS mean kinetic energy (1.45 eV) 10 cm away from the target at 0.7 Pa. However, this condition is challenging to reproduce experimentally.

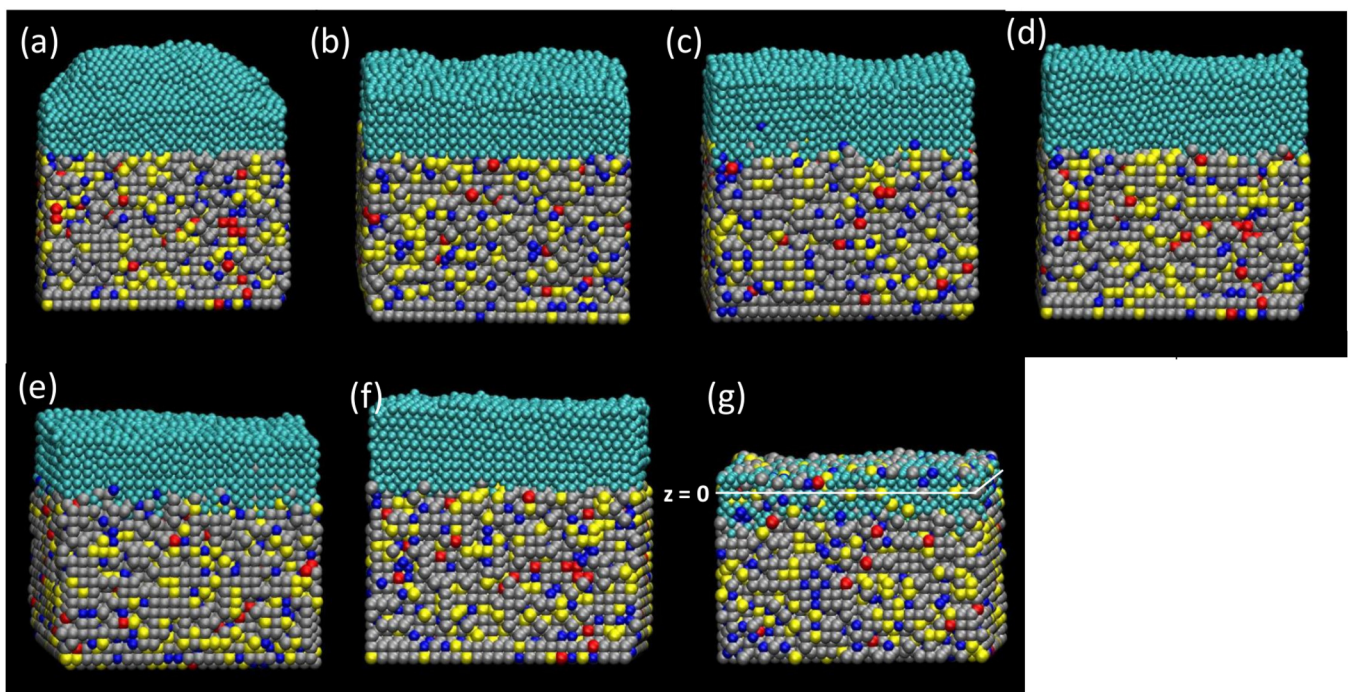


FIG. 4. Snapshots of the simulated films after 40 ns: (a) Cu beamlike at $\mathcal{E}_n = 1.45$ eV, (b) thermal evaporation, (c) dcMS, (d) HiPIMS 90% Cu-10% Cu⁺, (e) bipolar HiPIMS +180 V 90% Cu-10% Cu⁺, (f) HiPIMS 50% Cu-50% Cu⁺, and (g) bipolar HiPIMS +180 V 50% Cu-50% Cu⁺. The location indicated as $z = 0$ is the initial substrate surface. Color code: cyan Cu, yellow Cr, silver Fe, red Mo, and blue Ni.

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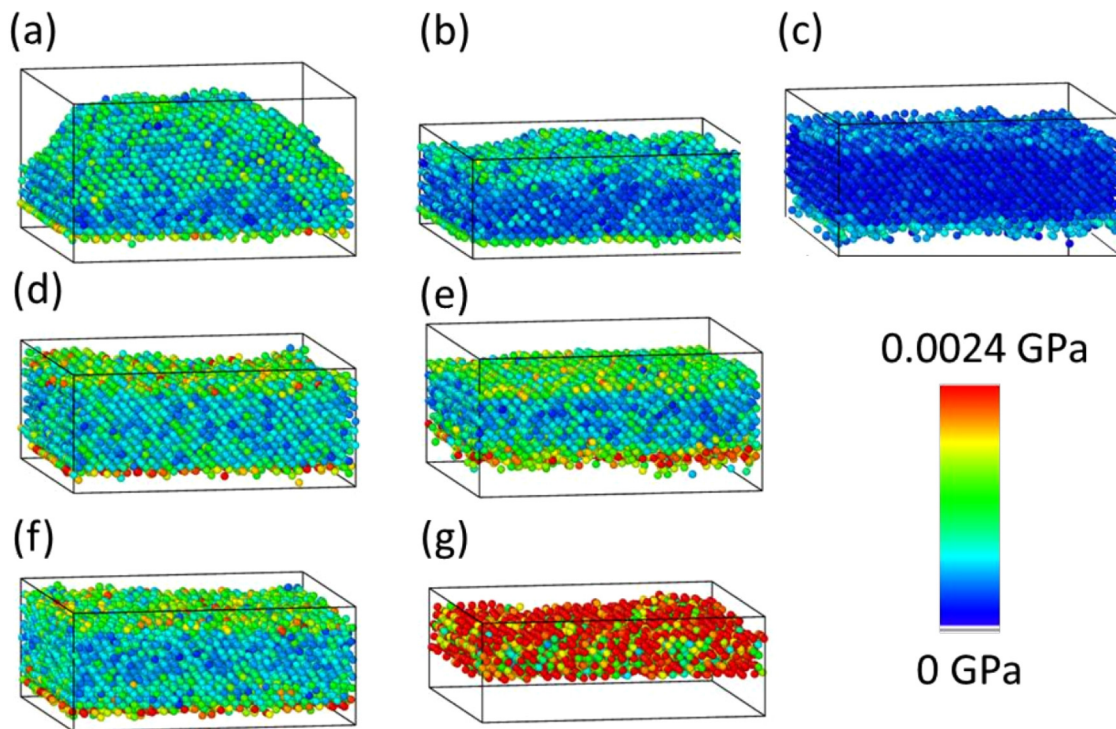
TABLE I. Cu film properties derived from the simulated films.

	Cu sticking coefficient	Substrate erosion rate (%)	Interface height (nm)	Film structure (% fcc)	RMS roughness ^a (nm)
Monoenergetic Cu atom beam	0.98	<0.01	0	60	1.45
Thermal evaporation	0.76	0	0	50	0.56
dcMS	0.86	0.3	0.5	48	0.57
HiPIMS 10% Cu ⁺	0.91	0.01	0.3	54	0.59
Bipolar HiPIMS +180 V and 10% Cu ⁺	0.79	0.5	1.5	57	0.56
HiPIMS 50% Cu ⁺	0.94	0	0.5	42	0.53
Bipolar HiPIMS +180 V and 50% Cu ⁺	0.42	1	5	8	0.23

^aRoot mean square (RMS) roughness $R = \frac{1}{N} \sqrt{\sum (|z^2 - \langle z \rangle|^2)}$.

The next highest crystallinity was obtained for bipolar HiPIMS (+180 V 10% Cu⁺), also providing a non-negligible mixing interface that is expected to improve film adhesion [Fig. 4(e)]. Regular HiPIMS (10% Cu⁺) without a secondary positive pulse showed a similar film quality, but the interface mixing was reduced [Fig. 4(d)]. Both have high sticking coefficients. Thermally evaporated and dcMS-deposited films exhibited similar film quality (50% fcc), but thermal evaporation showed a sticking coefficient

that was 13% lower. The high ion rate in bipolar HiPIMS allows for large layer mixing, but at the expense of low Cu sticking owing to film self-sputtering.²³ Additionally, it exhibited the largest substrate erosion rate (1%), whereas it was marginal for all the other processes. The rms roughness, reported in Table I, is the highest for constant energy beam deposition. Regular HiPIMS with 90% Cu-10% Cu⁺ exhibits only slightly higher roughness than thermal evaporation and dcMS deposition. The most aggressive



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FIG. 5. Atomic virial stress in the films deposited via the various PVD process: (a) Cu beamlike at $\mathcal{E}_n = 1.45$ eV, (b) thermal evaporation, (c) dcMS, (d) HiPIMS 90% Cu-10% Cu⁺, (e) bipolar HiPIMS +180 V 90% Cu-10% Cu⁺, (f) HiPIMS 50% Cu-50% Cu⁺, and (g) bipolar HiPIMS +180 V 50% Cu-50% Cu⁺. The substrate atoms have been removed for clarity.

(bipolar HiPIMS +180 V and 50% Cu⁺) leads to very low roughness but with almost no film growth due to self-sputtering. Therefore, it seems that bipolar HiPIMS with low ion content reduces roughness. Therefore, for regular HiPIMS, to reduce roughness, it is preferable to have higher ion flux, while with bipolar HiPIMS, low ion flux and a high positive bias are preferred. Note that the simulated films are around 3 nm thick. Experimental rms surface roughness values for HiPIMS deposited copper films, determined by an AFM (atomic force microscope), are in the range of 3.6–6.4 nm²⁴ and 1.3–3.9 nm,²⁵ depending on the surface bias, and 1.8–5.8 nm, depending on the pulse width.²⁶ For dc magnetron sputter deposition values of 11 nm have been reported.²⁶ All the experimentally deposited films have thickness above 120 nm. The difference in the rms roughness values between experiments and MD simulations is due to the thickness difference.

Atomic stress is an important property for comparing films deposited by the different processes.^{27,28} The calculated atomic virial stress²⁹ is expressed as

$$\sigma_i = -m_i \frac{d}{dt} \vec{u}_i \times \frac{d}{dt} \vec{u}_i + \frac{1}{2} \sum_{j \neq i} \vec{r}_{ij} \times \vec{f}_{ij}, \quad (2)$$

where i and j are atom indices and \vec{f}_{ij} is the interatomic force between atoms j and i . The summation is over all neighboring atoms within the force cutoff, m_i is the mass of atom i , \vec{u}_i is the displacement vector of atom i relative to a reference position, $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$, and \times is the tensor product of the two vectors. In Fig. 5, the stress magnitude of each atom (represented by a sphere) is demonstrated by the color map for the films drawn in Fig. 4. The substrate has been removed for clarity. The dcMS-deposited film [Fig. 5(c)] exhibits the lowest stress, while the highest stress is obtained for the +180 V bipolar HiPIMS deposited film with 50% Cu⁺ [Fig. 5(g)].

The beamlike deposition [Fig. 5(a)] did not display a high stress, but the roughness was the highest. The thermal evaporation deposited film exhibits low stress [Fig. 5(b)]. The three HiPIMS deposited films shown in Figs. 5(d)–5(f) provide reasonably low stress compared to the dcMS-deposited film. It should be noted that more stressed atoms are present at the interface with the substrate. The bipolar HiPIMS (+180 V and 50% Cu⁺) deposited film [Fig. 5(e)] shows less stress in the inner film than the other HiPIMS deposited films. This means that bipolar HiPIMS can provide a relaxed film. This has to be linked to the highest degree of crystal ordering, as shown in Table I, where the fcc fraction reached 57%.

V. SUMMARY

In summary, molecular dynamics simulations of various PVD processes can be handled and differentiated using the corresponding AEDs and IEDs of sputtered atoms and ions. It is possible to use the experimental IEDs obtained by energy-resolved mass spectrometry. This allows for a better account of the process characteristics. In the present case of Cu deposition, bipolar HiPIMS (+180 V and 10% Cu⁺ ions) exhibited the best film properties in terms of crystallinity and atomic stress among the PVD processes investigated.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Soumya Atmane: Data curation (equal); Formal analysis (equal); Investigation (equal); Validation (equal); Writing – review & editing (equal). **Alexandre Maroussiak:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Software (equal); Writing – review & editing (equal). **Amaël Caillard:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal). **Anne-Lise Thomann:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Methodology (equal); Resources (equal); Writing – review & editing (equal). **Movaffaq Kateb:** Conceptualization (equal); Formal analysis (equal); Validation (equal); Writing – review & editing (equal). **Jon Tomas Gudmundsson:** Conceptualization (equal); Formal analysis (equal); Validation (equal); Writing – review & editing (equal). **Pascal Brault:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

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