

# Single atom Ru-supported reduced graphene oxide integrated self-assembled monolayer as a nm-scale Cu diffusion barrier

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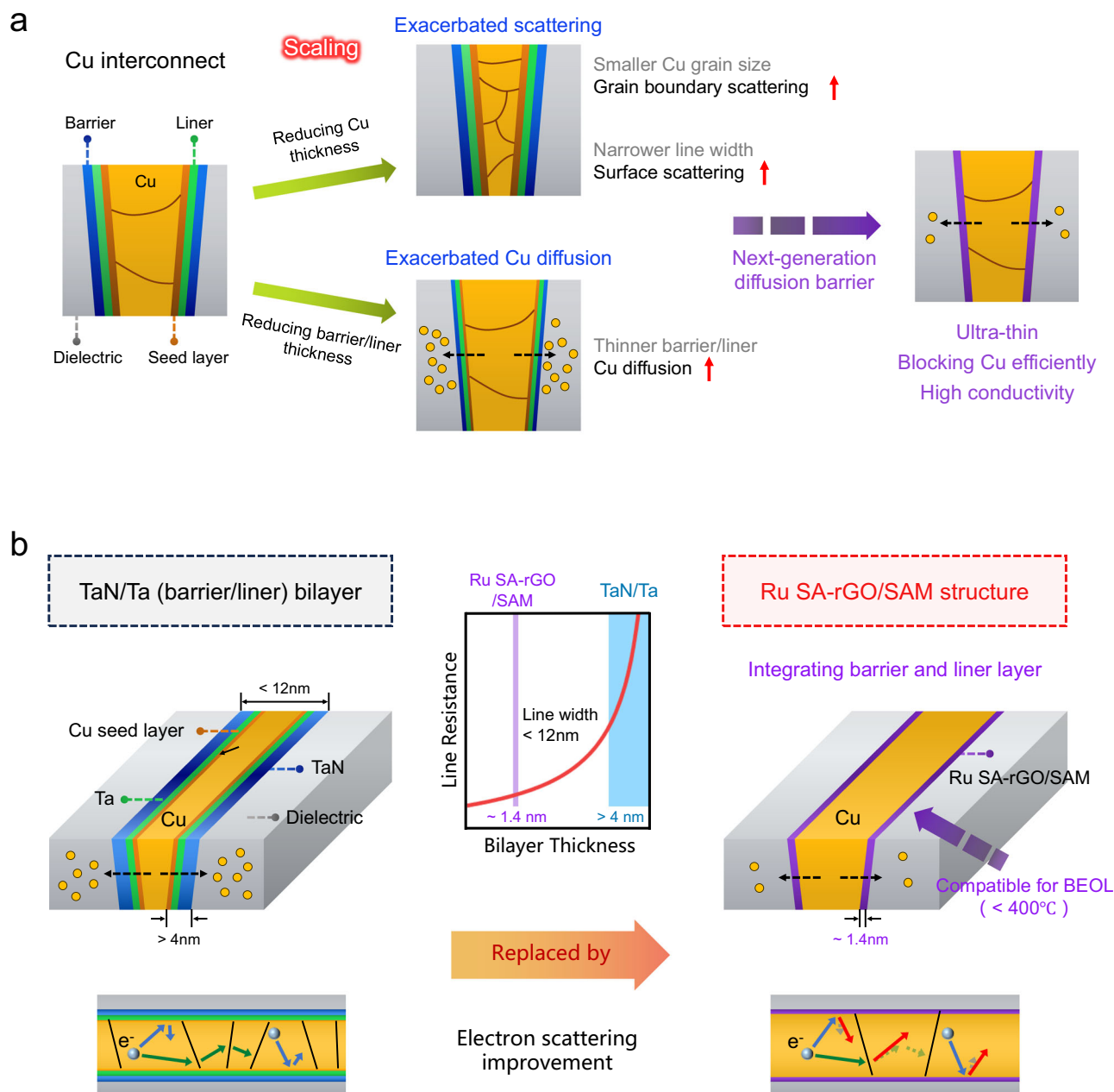
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In advanced integrated circuits, signal transmission delay arising from interconnect resistance is a main problem hindering the development of electronic devices, while the conventional several-nanometer-thick TaN/Ta barrier with high resistivity causes a surge in interconnect resistance due to the size effect. To address this issue, it is crucial to develop Cu barrier materials. Here, we design an integrated ultra-thin Cu diffusion barrier (~1.4 nm) consisting of single-atom Ru-supported reduced graphene oxide (Ru SA-rGO) and self-assembled monolayer (SAM) derived from (3-aminopropyl)triethoxysilane, which combines the dual functions of liner and barrier. The supporting of Ru requires N-doping as a bridge. Remarkably, the mean time-to-failure of devices with Ru SA-rGO/SAM is approximately 24 times longer than barrier-free devices. Ru atoms can both physically block Cu diffusion by filling rGO vacancies and chemically capture Cu through enhanced adsorption. Our work provides insight into diffusion barrier development in advanced Cu interconnects.

Under the post Moore era, as chip integration continues to increase in the Integrated Circuit (IC) industry, the feature size of interconnects has been shrinking continuously<sup>1</sup>. The pivotal factor limiting the performance of electronic devices is no longer the processing speed of transistors, but rather the issues of signal transmission delay and reliability arising from interconnects<sup>2,3</sup>. The barrier/liner (TaN/Ta) bilayer, composed of TaN with strong ability to block Cu diffusion and Ta with effective adhesion to Cu, has been widely used in interconnects for a considerable period<sup>4,5</sup>. Nevertheless, as the interconnection line width decreases, the proportion of TaN/Ta occupying the total cross-sectional area of the interconnect continues to increase. Consequently, the high resistivity of TaN/Ta becomes increasingly detrimental to the line conductivity, leading to severe signal transmission delay<sup>6–8</sup>. Therefore, research needs to be conducted on new interconnect barrier materials that can fulfill three key criteria: ultra-thin, high conductivity, and excellent diffusion barrier property (Fig. 1a)<sup>9,10</sup>.

In recent years, researchers have focused on and conducted extensive studies in three main directions for diffusion barriers: self-forming alloys<sup>11,12</sup>, self-assembled monolayers (SAM)<sup>13,14</sup>, and two-dimensional (2D) materials<sup>15–19</sup>. It has been demonstrated that both the alkyl chain and the terminal group of the SAM have a crucial influence on its diffusion barrier properties<sup>20–25</sup>. Caro et al. found that a NH<sub>2</sub>-terminated SAM derived from (3-aminopropyl)trimethoxysilane (APTMS) exhibited the best compatibility for Cu interconnects among the analyzed SAMs with a variety of terminal groups and chain lengths<sup>20</sup>. Further studies have shown that by chemically modifying the terminal groups of APTMS or coupling it with other molecules, the diffusion barrier properties, adhesion to Cu, and conductivity of the resulting SAMs can be respectively enhanced<sup>23–25</sup>. Generally, SAMs on SiO<sub>2</sub> can achieve an ultra-thin film of less than 1 nm while maintaining satisfactory uniformity and continuity. However, SAMs start to desorb from SiO<sub>2</sub> (250 °C) or even decompose (350 °C) below the operating temperature for back-end-of-line (BEOL) process<sup>26,27</sup>. This low thermal

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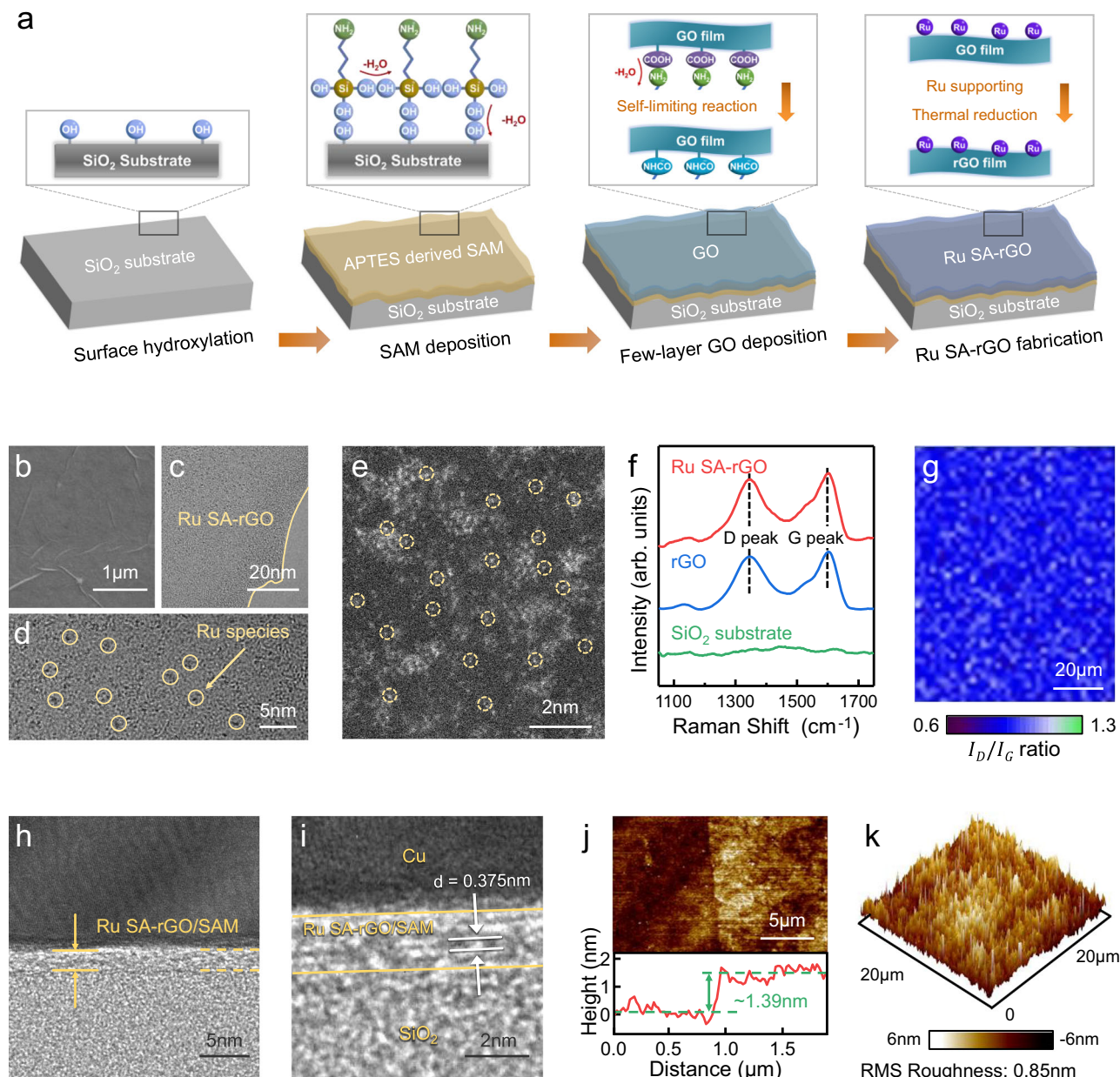
**Fig. 1 | The challenges posed by the scaling of Cu interconnect and the requirements for the materials available for the next-generation diffusion barrier. a** The schematic diagram representative of the damascene structure of Cu interconnect. **b** Comparison between the diffusion barrier fabricated in this work

(Ru SA-rGO/SAM structure) and the conventional TaN/Ta bilayer. The diffusion barrier presented in this work simultaneously meets the requirements of ultra-thin, excellent diffusion barrier properties, high conductivity, and compatibility with BEOL process.

stability of SAMs may significantly damage the interconnection performance.

2D materials have the potential to be the next-generation interconnect barrier due to their distinctive structural characteristics<sup>10</sup>, such as graphene<sup>15,28,29</sup>, hexagonal boron nitride (h-BN)<sup>16,30</sup>, and transition metal dichalcogenides (TMDs)<sup>19–21</sup>. Among these 2D materials, graphene stands out because of its ultrahigh carrier mobility<sup>31</sup>. The graphene-copper integrated structure facilitates charge transfer at the interface, effectively enhancing interconnect conductivity<sup>32–34</sup>. Furthermore, graphene has excellent properties to block vertical Cu diffusion<sup>35,36</sup>. Research by Li et al. demonstrated that single-layer graphene with a thickness of 0.35 nm exhibits diffusion barrier property comparable to 4 nm TaN<sup>28</sup>. Additionally, graphene exhibits high thermal stability against Cu diffusion. Even under thermal stress

conditions of 700 °C for 30 min, thermal diffusion does not occur in 1 nm thick tri-layer graphene<sup>15</sup>. For a long time, the high growth temperature of graphene during chemical vapor deposition (CVD), along with macroscopical transfer defects, such as folds, cracks and tears, have presented challenges in applying graphene as a diffusion barrier in BEOL processes<sup>10,37–41</sup>. Recent researches have shown that graphene can now be directly deposited on SiO<sub>2</sub> at a low temperature<sup>42</sup>, and the stacking of wafer-scale ultra-flat graphene with scarce transfer defects has been achieved through flat-to-flat transfer process<sup>43</sup>. However, graphene exhibits poor adhesion to Cu due to its intrinsic weak van der Waals interaction between layers<sup>10,44</sup>. Moreover, the rapid migration of Cu atoms or ions between graphene layers limits the improvement of its diffusion barrier properties, especially when increasing the number of graphene stacking



**Fig. 2 | Synthesis and Characterization of Single Atom Ru-supported (Ru SA)-rGO/SAM.** **a** Synthesis strategy of Ru SA-rGO/SAM structure. **b** SEM, **c** TEM, **d** HRTEM and **e** HAADF-STEM images of Ru SA-rGO. **f** Raman spectra including SiO<sub>2</sub> substrate, pristine rGO and Ru SA-rGO. **g** Raman mapping of the  $I_D/I_G$  ratio of Ru

SA-rGO. **h** TEM and **i** HRTEM images of the cross section of Ru SA-rGO/SAM. **j** AFM image of Ru SA-rGO/SAM, measuring its thickness to be ~1.39 nm. **k** AFM 3D image of Ru SA-rGO/SAM, measuring its RMS roughness to be 0.85 nm. Source data are provided as a Source Data file.

layers<sup>28</sup>. These factors restrict the potential application of graphene as a diffusion barrier.

In this work, we designed an integrated diffusion barrier structure consisting of a single-atom Ru-supported reduced graphene oxide (Ru SA-rGO) and a SAM derived from (3-aminopropyl)triethoxysilane (APTES). Compared to graphene, graphene oxide (GO) introduces numerous oxygen-containing functional groups at its surface and edges<sup>45</sup>, which enable a stable combination between GO and SAM through reaction with the terminal groups in SAM<sup>46</sup>. Through the support of Ru species on GO/SAM, combined with a subsequent thermal reduction process, the Ru SA-rGO/SAM structure was successfully synthesized in a BEOL-compatible temperature. The results indicate that the Ru SA-rGO/SAM structure, integrates the dual functions of liner and diffusion barrier with its ultra-thin thickness, achieving a combination of good adhesion to Cu and excellent

thermal/electrical diffusion barrier properties. Moreover, the critical role of Ru in the superior properties of Ru SA-rGO/SAM has been verified through calculations. It can be expected that the ultra-thin Ru SA-rGO/SAM diffusion barrier can significantly benefit the interconnect performance (Fig. 1b).

## Results

### Synthesis and characterization of Ru SA-rGO/SAM

Figure 2a illustrates the synthesis process of Ru SA-rGO/SAM structure on SiO<sub>2</sub> substrate. Firstly, surface-hydroxylated SiO<sub>2</sub> was achieved through Piranha solution etching. Molecule adsorption was then carried out via hydrogen bonding between hydrolyzed APTES and surface-hydroxylated SiO<sub>2</sub>, followed by a transformation from the initial hydrogen bonding to strong covalent bonding through dehydration reaction<sup>47</sup>. After the deposition of an atomic-scale thickness



SAM, a uniform few-layer GO was fabricated on it through an electro-assisted self-limiting deposition process<sup>48</sup>. The reaction between the carboxyl groups (-COOH) in GO and the amino terminal groups (-NH<sub>2</sub>) in APTES contributes to the self-limiting deposition. Scanning electron microscopy (SEM) image of few-layer GO deposited on SAM was observed in supplementary Fig. 1, where the wrinkled feature represents the stacking morphology of GO. The support of Ru species onto GO requires a N-doping process as a bridge. As the nitrogen source, aniline firstly stacked on GO through  $\pi$ - $\pi$  interactions using edge-to-face model<sup>49</sup>. Ru species were then coordinated with the -NH<sub>2</sub> of aniline. Through a final thermal reduction process, the N species were inserted into the GO skeleton while the Ru species were immobilized by complexation reaction. The SEM image of the fabricated Ru-supported rGO is shown in Fig. 2b.

The morphology of Ru-supported rGO was characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As shown in Fig. 2c, Ru species, appearing as black dots in the TEM image, were well-dispersed on the surface of GO. In the HRTEM image (Fig. 2d), the supported Ru species (highlighted by yellow circles) exhibit lattice fringes that are significantly distinct from the surrounding GO matrix, demonstrating the successful support of Ru species on GO. To further explore the support configuration of Ru species, high-angle annular dark-field scanning TEM (HAADF-STEM) was employed. Due to the contrast in HAADF-STEM being proportional to the square of the atomic number ( $Z^2$ ), the Ru species possess remarkably higher contrast compared to the C and N species in the matrix. The distribution of numerous discrete bright spots seen in Fig. 2e indicates that the Ru species were supported as individual single atoms.

Figure 2f shows the comparison of Raman spectra between SiO<sub>2</sub> substrate and the Ru SA-rGO fabricated on this substrate. The Ru SA-rGO exhibits two prominent Raman peaks at 1346 and 1604 cm<sup>-1</sup>, which are well-matched with the D and G bands of graphene, respectively. In contrast, the SiO<sub>2</sub> substrate lacks these peaks. The D-to-G band intensity ratio ( $I_D/I_G$ ) is widely recognized as an important parameter for evaluating the defect density and degree of graphitization in carbonaceous materials<sup>50</sup>. As shown in Fig. 2g, the  $I_D/I_G$  of Ru SA-rGO is concentrated around 0.85. This demonstrates the uniformity of the fabricated Ru SA-rGO, yet it does not exhibit a high degree of graphitization, which verifies the mostly amorphous tendency observed in the TEM images.

Figure 2h, i reveal the cross-sectional morphology of Ru SA-rGO/SAM structure. In the TEM image (Fig. 2h), the Ru SA-rGO/SAM layer on SiO<sub>2</sub> substrate exhibits a tightly adhered interface with no noticeable protrusions or unevenness. As shown in Fig. 2i, compared to the regular lattice fringes of graphene, the lattice fringes exhibited by Ru SA-rGO mostly tend to be amorphous. This amorphous characteristic of Ru SA-rGO ensures its ability to block the lateral migration of Cu as a diffusion barrier. The interplanar spacing of Ru SA-rGO analyzed by fast Fourier transform (FFT) is about 0.375 nm, which is slightly higher than the interplanar spacing of rGO (-0.35 nm)<sup>51</sup>. This may be due to the support of Ru atoms on rGO, whose atomic volume much larger than that of carbon.

The thickness and roughness of Ru SA-rGO/SAM were directly measured by atomic force microscopy (AFM). As shown in Fig. 2j, the thickness of Ru SA-rGO/SAM is approximately 1.39 nm, which includes a 0.37 nm SAM confirmed by ellipsometer. Meanwhile, the root mean square (RMS) roughness of Ru SA-rGO/SAM was determined to be 0.85 nm over a 20 × 20  $\mu$ m measurement area (Fig. 2k). To verify the uniformity of the diffusion barrier, we fabricated a 20 × 20 mm Ru SA-rGO/SAM/SiO<sub>2</sub> sample and performed AFM analysis across five distinct regions (20 × 20  $\mu$ m measurement area), as shown in supplementary Fig. 3. The results reveal consistent roughness values averaging 0.87 nm with only 0.091 nm variation between maximum and minimum measurements, demonstrating

high macroscopic uniformity of Ru SA-rGO/SAM throughout the sample.

To clarify the configuration of N and Ru species in Ru SA-rGO/SAM, X-ray photoelectron spectroscopy (XPS) was employed on SAM, N-rGO/SAM (only conducted N-doping process), and Ru SA-rGO/SAM (conducted both N-doping and Ru-supporting process). The N-doping process typically introduces four distinct N-containing species: pyridinic N, pyrrolic N, graphitic N and oxidized N, whose configurations are shown in Fig. 3a<sup>52</sup>. Graphitic N mainly fills the point defects in rGO, while pyridinic N and pyrrolic N can repair larger vacancies or establish connections at the edges of rGO.

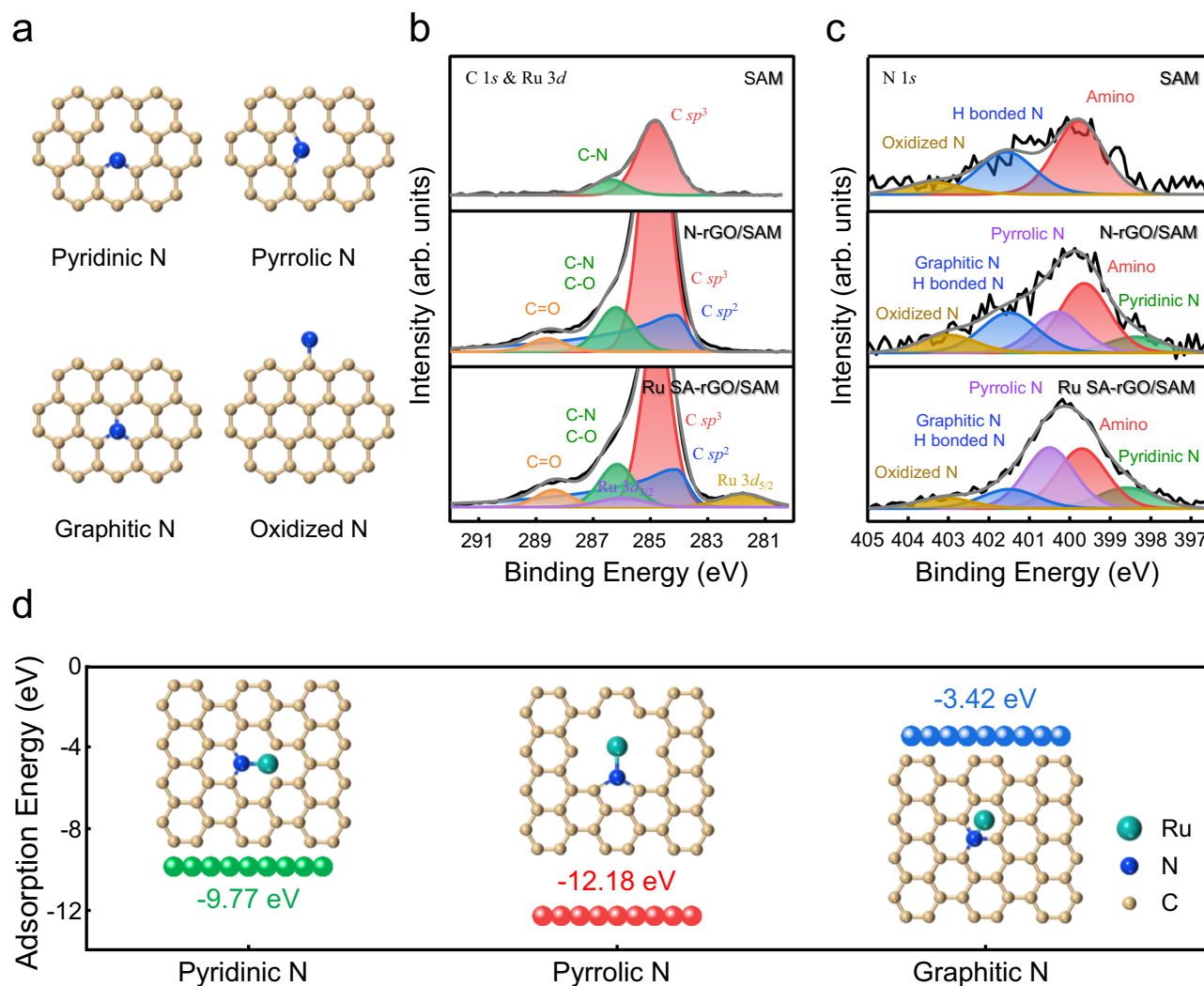
The C 1s spectra of the three samples are shown in Fig. 3b. Notably, a small peak can be clearly observed at a position deviating from the main C 1s spectra of Ru SA-rGO/SAM, which can be attributed to the Ru 3d spectra. The successful supporting of Ru species can be further validated by the appearance of the Ru 3p peak in the XPS survey spectra (supplementary Fig. 6). The Ru 3d<sub>5/2</sub> peak of Ru SA-rGO/SAM at 281.8 eV is situated between Ru<sup>0</sup> (279.75 eV) and Ru<sup>+3</sup> (282.4 eV)<sup>53</sup>. It is suggested that the valence state of the supported Ru is between 0 and +3. Additionally, the much lower intensity of the Ru 3d<sub>5/2</sub> peak compared to the C 1s peaks indicates a low content of Ru supported on rGO.

As shown in Fig. 3c, the N 1s spectra of SAM reveals three distinct peaks, corresponding to amino at 399.7 eV, hydrogen-bonded nitrogen (H-bonded N) at 401.5 eV, and oxidized N at 403.3 eV, respectively<sup>25</sup>. The strong peak of H-bonded N might originate from the hydrogen bonding between amino groups in APTES with each other or with hydroxyl groups on SiO<sub>2</sub> substrate<sup>13</sup>. In contrast, the N 1s spectra of N-rGO/SAM and Ru SA-rGO/SAM exhibit three new components, which are assigned to indexed to pyridinic N (398.4 eV), pyrrolic N (400.3 eV), graphitic N (401.5 eV)<sup>52</sup>.

To further investigate the interaction between Ru and N species in rGO, we conducted a comprehensive analysis of XPS peak positions. Compared to N-rGO/SAM, the binding energy of pyridinic N and pyrrolic N in Ru SA-rGO/SAM shifts 0.2 eV higher, while the binding energy of amino and graphitic N remains unchanged (supplementary Table 1). This indicates that pyridinic N and pyrrolic N play a role in coordinating with Ru atoms, leading to a change in their electronic state, while amino and graphitic N scarcely participate in the coordination<sup>13</sup>. Meanwhile, the binding energies of the C  $sp^2$  and C  $sp^3$  peaks in the C 1s spectra also show no change (supplementary Table 2). This reveals that very few Ru atoms are adsorbed on the lattice of rGO. The adsorption energy ( $\Delta E_{\text{ads}}$ ) results from density functional theory (DFT) calculations further support this conclusion, as shown in Fig. 3d. A more negative  $\Delta E_{\text{ads}}$  indicates a higher tendency for Ru atoms to be adsorbed on the specific N-doped structures. Compared to graphitic N (-3.42 eV), Ru atoms exhibit much lower  $\Delta E_{\text{ads}}$  for pyridinic N (-9.77 eV) and pyrrolic N (-12.18 eV), indicating the preferential adsorption of Ru atoms on pyridinic N and pyrrolic N. Furthermore, the optimized structure shows that Ru atoms tend to be located at the vacancies within the plane of rGO when adsorbed on pyridinic N and pyrrolic N. This suggests that the supported Ru atoms can effectively fill the defects in rGO. Ru atoms were replaced by Cu atoms to calculate  $\Delta E_{\text{ads}}$  under the same structures. The results show that the  $\Delta E_{\text{ads}}$  of Cu atoms is significantly more positive than that of Ru atoms in each N-doped structure, which proves that the supported Ru will not desorb due to the introduction of Cu (supplementary Fig. 7 and 8).

### Adhesion to Cu

The tape test method was employed to verify the adhesion of Cu on Ru SA-rGO/SAM. After successfully preparing Ru SA-rGO/SAM on a SiO<sub>2</sub> substrate, a ~ 25 nm Cu film was deposited by vacuum evaporation. The adhesion test was conducted using 3 M tape by contacting and then removing it. After the removal of the 3 M tape, the Cu film remained only in the regions with Ru SA-rGO/SAM, as shown in Fig. 4a and



**Fig. 3 | Identification of the configuration of N and Ru species in single atom Ru-supported (Ru SA)-rGO.** **a** Schematic diagram showing the configuration of nitrogen species doped into rGO lattice. **b** XPS C 1s spectra of SAM, N-rGO/SAM, and Ru SA-rGO/SAM (from top to bottom). **c** XPS N 1s spectra of SAM, N-rGO/SAM, and Ru SA-rGO/SAM (from top to bottom). **d** The optimized structures and the

adsorption energies for Ru-pyridinic N, Ru-pyrrolic N and Ru-graphitic N configurations. The structures were optimized by DFT calculations within the generalized gradient approximation and GGA-PBE approximation, as implemented in the VASP package. Source data are provided as a Source Data file.

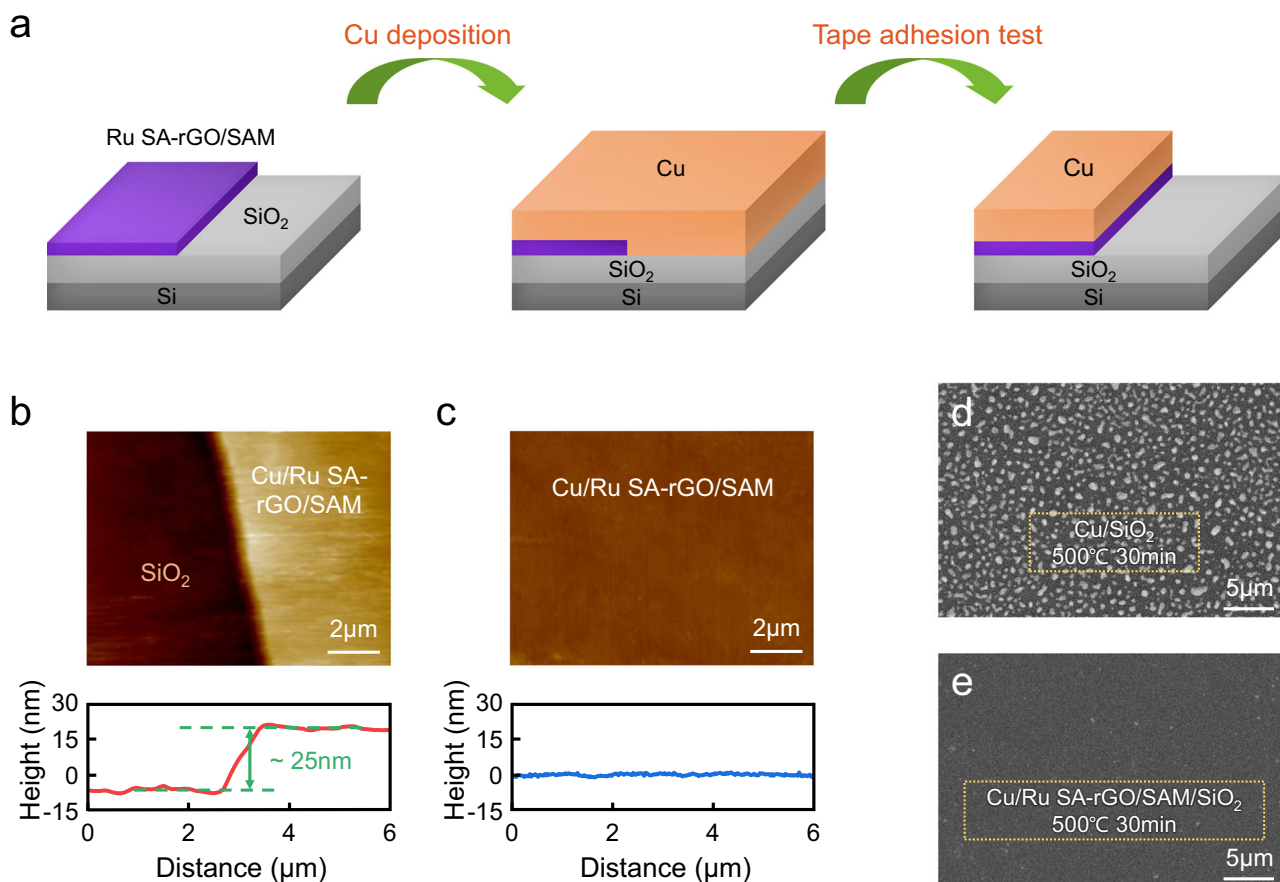
supplementary Fig. 9. AFM analysis indicates that after the tape adhesion test, the thickness difference at the interface with and without Ru SA-rGO/SAM is approximately 25 nm (Fig. 4b), which corresponds to the deposited thickness of the Cu film. In addition, the Cu film deposited on Ru SA-rGO/SAM shows no significant thickness fluctuations after the tape adhesion test, as shown in Fig. 4c. These results suggest that the Cu film deposited on the Ru SA-rGO/SAM layer was almost unaffected by the tape.

After annealing the samples at 500 °C for 30 min, it was observed that the Cu film deposited on the SiO<sub>2</sub> substrate cracked and aggregated into numerous spherical particles, as shown in Fig. 4d (The SEM images of the samples before annealing are shown in supplementary Fig. 10). In contrast, the sample with Ru SA-rGO/SAM maintained the integrity of the Cu film due to its strong adhesion (Fig. 4e). We deposited thicker Cu films (~1 μm) on samples with and without Ru SA-rGO/SAM, and further examined the interface adhesion using cross-sectional SEM. The interface between Ru SA-rGO/SAM and the Cu film is tightly bonded (supplementary Fig. 11b), whereas there is a noticeable separation between the substrate without Ru SA-rGO/SAM and the Cu film (supplementary Figs. 11a and 12). All the results indicate that the Ru SA-rGO/SAM layer exhibits excellent adhesion to Cu.

To quantitatively evaluate the interfacial adhesion strength, four-point bending tests were performed for both Cu/SiO<sub>2</sub> and Cu/Ru SA-rGO/SAM/SiO<sub>2</sub> structures. The load-displacement curves of both structures are shown in supplementary Fig. 13. The results indicate that the interfacial delamination occurred at 4.07 N for Cu/SiO<sub>2</sub> and at 6.08 N for Cu/Ru SA-rGO/SAM/SiO<sub>2</sub>. We further quantitatively evaluate the interfacial adhesion energy of the two structures based on the calculation equation for interfacial adhesion energy ( $G_c$ )<sup>54</sup>

$$G_c = \frac{21(1 - \nu_s^2)P_c^2 L^2}{16E_s B^2 h^3} \quad (1)$$

where  $P_c$  is the critical load for interface delamination,  $L$  is the distance between the loading and supporting points (7 mm),  $B$  is specimen width (5 mm),  $h$  is substrate thickness (525 μm),  $E_s$  is Young's modulus (130 GPa), and  $\nu_s$  is Poisson's ratio (0.28). The calculated  $G_c$  values of both configurations are displayed in supplementary Table 3. The result reveals a significant increase from 2.1 to 4.7 J m<sup>-2</sup> after the introduction of Ru SA-rGO/SAM, which effectively validates enhanced interfacial adhesion.



**Fig. 4 | Adhesion of single atom Ru-supported (Ru SA)-rGO/SAM to Cu.**

**a** Schematic diagram of tape adhesion test. **b** AFM image of the interface between Cu/Ru SA-rGO/SAM and SiO<sub>2</sub>. **c** AFM image of the Cu/Ru SA-rGO/SAM structure.

SEM images of **d** Cu/SiO<sub>2</sub> and **e** Cu/Ru SA-rGO/SAM/SiO<sub>2</sub> after annealing at 500 °C for 30 min. Source data are provided as a Source Data file.

### Thermal stability and ability to block Cu thermal diffusion

To evaluate the thermal stability of Ru SA-rGO/SAM structure and its ability to block Cu thermal diffusion, a 50 nm-thick Cu film was deposited on a Ru SA-rGO/SAM/SiO<sub>2</sub>/Si sample. For comparison, in addition to directly depositing 50 nm Cu film on SiO<sub>2</sub>/Si without diffusion barrier, we also prepared samples with a diffusion barrier of a single SAM or pristine rGO/SAM, respectively. All samples were annealed at temperatures ranging from 400 °C to 600 °C for 30 min in an argon atmosphere. The thermal diffusion failure mechanism of Cu interconnects is shown in Fig. 5a. For samples without diffusion barrier, Cu atoms may easily infiltrate into the dielectric as the temperature increases. Subsequently, Cu reacts with Si to form intermetallic compounds (Cu<sub>x</sub>Si<sub>y</sub>) at the interface, leading to ultimate failure of devices. In contrast, the addition of a diffusion barrier can significantly suppress Cu diffusion, thereby delaying failure arising from the formation of Cu<sub>x</sub>Si<sub>y</sub><sup>15</sup>.

After annealing the Cu/Ru SA-rGO/SAM/SiO<sub>2</sub> structure at 600 °C for 30 min, cross-sectional observation (Fig. 5b) indicates that the Ru SA-rGO/SAM layer remained intact, with no significant formation of Cu<sub>x</sub>Si<sub>y</sub> intermetallic compounds at the interface. STEM-energy dispersive X-ray spectroscopy (STEM-EDS) further confirms that, due to the presence of the Ru SA-rGO/SAM diffusion barrier, there was negligible diffusion of Cu atoms into the SiO<sub>2</sub> during annealing (Fig. 5c–f). These results demonstrate that the Ru SA-rGO/SAM diffusion barrier exhibits excellent thermal stability and remarkable resistance to Cu thermal diffusion.

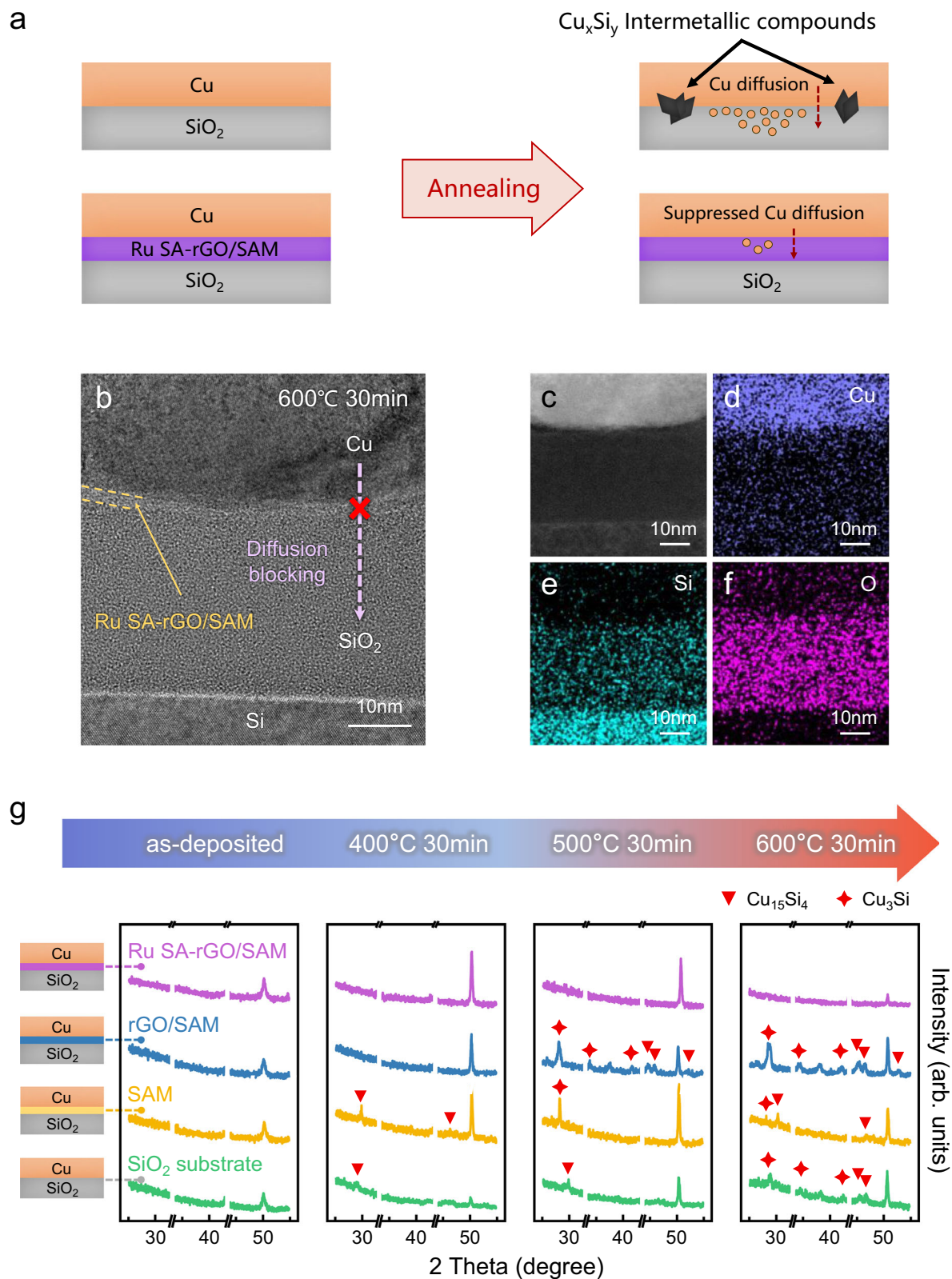
According to the failure mechanism, X-ray diffraction (XRD) analysis was conducted for phase identification. Figure. 5g illustrates

the variation of XRD patterns for samples with different diffusion barriers in various annealing conditions. Except for the diffraction peaks of substrate, it can be easily observed that two types of intermetallic compounds, Cu<sub>3</sub>Si and Cu<sub>15</sub>Si<sub>4</sub>, were generated during the annealing process. The diffraction peaks at 27.9°, 35.2°, 42.4°, and 49.5°, are respectively identified as (020), (021), (030), and (301) of Cu<sub>3</sub>Si, while diffraction peaks at 29.4°, 46.1°, 48.1°, and 53.7°, are respectively indexed as (310), (422), (510), and (440) of Cu<sub>15</sub>Si<sub>4</sub><sup>15,55,56</sup>. After annealing at 400 °C for 30 min, Cu<sub>x</sub>Si<sub>y</sub> peaks start to appear in samples without diffusion barrier and only with SAM diffusion barrier, which proves the low thermal stability of SAM. As the temperature rises to 500 °C, the rGO/SAM diffusion barrier quickly fails, accompanied by the extensive formation of Cu<sub>x</sub>Si<sub>y</sub>. Only the samples with Ru SA-rGO/SAM diffusion barrier still retain the ability to block Cu diffusion at 600 °C (Ru SA-rGO/SAM starts to fail at 700 °C, as shown in supplementary Fig. 14). This indicates that the Ru-supporting process is a key factor contributing to the excellent ability of Ru SA-rGO/SAM diffusion barrier to block Cu diffusion.

### Electrical diffusion barrier properties

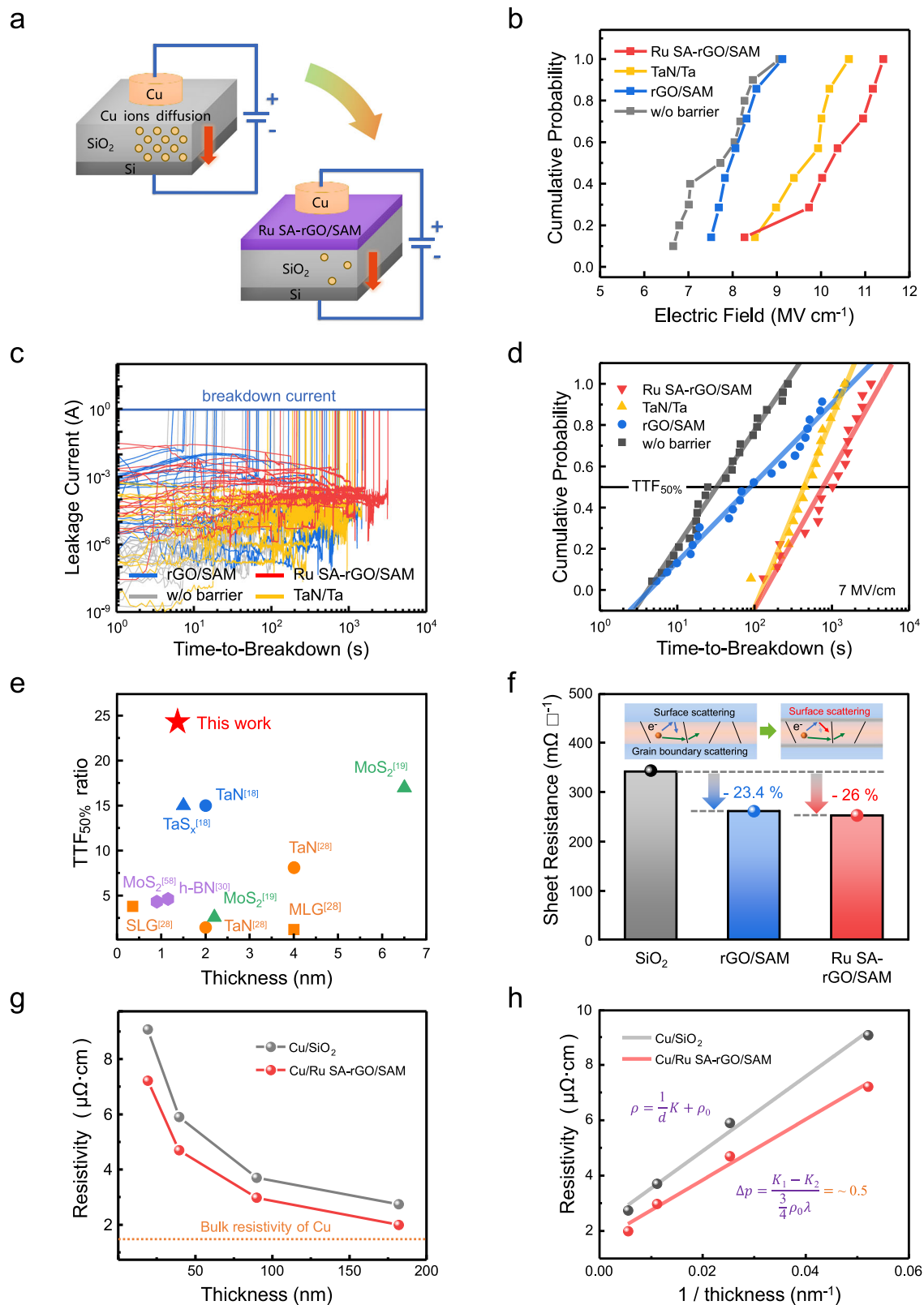
The electrical properties of the Ru SA-rGO/SAM structure were evaluated by electrical tests, including current-voltage (I-V) measurements and time-dependent dielectric breakdown (TDDB) measurements. To enable direct comparison of electrical diffusion barrier properties between Ru SA-rGO/SAM and TaN/Ta structure, we deposited a TaN/Ta bilayer with a total thickness of 6.27 nm on SiO<sub>2</sub> substrate, as illustrated in supplementary Fig. 15. For both electrical tests, a simplified metal-oxide-semiconductor (MOS) capacitor structure was prepared,





**Fig. 5 | Ability of single atom Ru-supported (Ru SA)-rGO/SAM to block Cu thermal diffusion.** **a** Schematic diagram of thermal diffusion failure mechanism of Cu interconnects. **b** HRTEM image, **c** HAADF-STEM image, and STEM-EDS mapping of **d** Cu, **e** Si and **f** O of the cross section of Cu/Ru SA-rGO/SAM/ $\text{SiO}_2$ /Si structure

after annealing at 600 °C for 30 min. **g** XRD patterns of samples including Cu/ $\text{SiO}_2$ , Cu/SAM/ $\text{SiO}_2$ , Cu/rGO/SAM/ $\text{SiO}_2$ , and Cu/Ru SA-rGO/SAM/ $\text{SiO}_2$  under different annealing conditions (As-deposited, 400 °C 30 min, 500 °C 30 min, and 600 °C 30 min). Source data are provided as a Source Data file.



as depicted in Fig. 6a. A vertical electric field was applied across the capacitor structure, driving the migration of Cu ions into the dielectric. As the electric field intensity increases or the time prolongs, a large number of Cu ions form conducting paths in the dielectric, causing breakdown failure of the capacitor structure<sup>37</sup>. The presence of a diffusion barrier can extend the lifetime of devices by preventing the migration of Cu ions.

I-V measurement indicates the variation of leakage current with the electric field intensity. It is considered as breakdown failure of devices when the leakage current abruptly jumps and exceeds a certain value. The voltage is recorded when the current jump occurs to evaluate the critical electric field ( $E_c$ ) of each device. We conducted I-V measurements on multiple devices with different diffusion barriers, and the variation of leakage current with the applied electric field is



**Fig. 6 | Electrical diffusion barrier properties and conductivity of single atom Ru-supported (Ru SA)-rGO/SAM. a** Schematic diagram of failure mechanism of Cu interconnects under electric field. **b** I-V measurement including devices without diffusion barrier and devices with rGO/SAM, TaN/Ta and Ru SA-rGO/SAM diffusion barrier. **c** Time-to-breakdown of devices tested by TDDB measurement. **d** Statistical distribution of time-to-breakdown of devices. **e** Comparison of TTF<sub>50%</sub> ratio and thickness of the Ru SA-rGO/SAM developed in this work with those reported in recent research (details shown in supplementary Table 5). **f** Sheet resistance of

devices with different diffusion barriers. **g** Resistivity of Cu films varying thicknesses (19.2 nm - 182 nm) on SiO<sub>2</sub> substrate and Ru SA-rGO/SAM. **h** Linear fitting of the resistivity ( $\rho$ ) versus inverse thickness ( $1/d$ ) relationship for Cu films on SiO<sub>2</sub> substrate and on Ru SA-rGO/SAM. The coefficients of determination ( $R^2$ ) are 0.99 for Cu/SiO<sub>2</sub> and 0.98 for Cu/Ru SA-rGO/SAM. By comparing the slope difference between two curves, the surface scattering parameter of the two structures are calculated to differ by  $\Delta p = -0.5$ . Source data are provided as a Source Data file.

shown in supplementary Fig. S16. The  $E_c$  values of devices were further plotted in Fig. 6b, and the cumulative probability represents the  $E_c$  values from low to high. Compared to devices without diffusion barrier (7.7 MV cm<sup>-1</sup>), devices with rGO/SAM (8.2 MV cm<sup>-1</sup>), TaN/Ta (9.7 MV cm<sup>-1</sup>), and Ru SA-rGO/SAM (10.3 MV cm<sup>-1</sup>) diffusion barriers correspond to an increase in the mean  $E_c$  value by 5.6%, 26.0%, and 33.1%, respectively.

TDDB measurement is used to evaluate the lifetime of devices at a constant electric field. The abrupt jump in leakage current indicates the breakdown failure of devices, similar to I-V measurement. Figure. 6c illustrates the variation of leakage current with the stress time under an electric field of 7 MV cm<sup>-1</sup>. It can be observed that although devices with TaN/Ta bilayer exhibit significantly longer time-to-breakdown overall compared to barrier-free devices, those featuring the Ru SA-rGO/SAM diffusion barrier show even longer time-to-breakdown. The statistical distribution of time-to-breakdown of devices is shown in Fig. 6d. For each type of devices, linear fitting was performed between the time-to-breakdown and cumulative probability. Each fitting presents great accuracy with a coefficient of determination ( $R^2$ ) above 0.95. Based on this, mean time-to-failure (TTF<sub>50%</sub>) was obtained by determining the time-to-breakdown corresponding to the cumulative probability of 0.5 for the fitting line, which serves as an overall evaluation of the lifetime of devices. Compared to the devices without diffusion barrier (~33 s), TTF<sub>50%</sub> is approximately 3, 14, and 24 times longer for devices with rGO/SAM (~91 s), TaN/Ta (~441 s), and Ru SA-rGO/SAM (~773 s) diffusion barrier, respectively. The results of TDDB measurement can be matched with those of IV measurement, collectively demonstrating that the Ru SA-rGO/SAM diffusion barrier exhibits superior electrical diffusion barrier performance compared to TaN/Ta bilayer. Additionally, similar to the thermal test results, all electrical test results reveal that the Ru-supporting process is the critical factor for achieving outstanding electrical properties.

Figure. 6e compares the TTF<sub>50%</sub> ratio and thickness in this work with those reported in recent research. Given the inconsistent electric field and temperature conditions used for TDDB measurement in different reports, the classic E-model is employed to normalize the data<sup>28</sup>

$$\text{TTF}_{50\%} \propto \exp\left(\frac{\Delta H_a}{k_b T} - \gamma E_s\right) \quad (2)$$

where  $\Delta H_a$  represents the activation energy of dielectric breakdown,  $k_b$  is the Boltzmann constant,  $\gamma$  is the electric field factor,  $E_s$  represents the electric field applied to the dielectric. The TTF<sub>50%</sub> value with  $E_s = 7 \text{ MV cm}^{-1}$ ,  $T = 298.15 \text{ K}$  is determined as the normalized TTF<sub>50%</sub> value. To compare the improvement in lifetime of devices by adding diffusion barrier, the ratio of the normalized TTF<sub>50%</sub> value of devices with each type of diffusion barrier to that of devices without diffusion barrier can be considered as a relative parameter to assess the diffusion barrier properties, which can be expressed as:

$$\text{TTF}_{50\%} \text{ ratio} = \frac{\text{TTF}_{50\%} \text{ with barrier}(7 \text{ MV cm}^{-1}, 25^\circ \text{C})}{\text{TTF}_{50\%} \text{ without barrier}(7 \text{ MV cm}^{-1}, 25^\circ \text{C})} \quad (3)$$

As shown in Fig. 6e and supplementary Table 5, the Ru SA-rGO/SAM diffusion barrier developed in this work exhibits significantly higher

TTF<sub>50%</sub> ratio compared to other reported diffusion barriers, while maintaining an ultra-thin thickness. This indicates that the Ru SA-rGO/SAM diffusion barrier is a candidate material for advanced Cu interconnect.

### Conductivity

To investigate the influence of different diffusion barriers on interconnect conductivity, Cu/diffusion barrier/SiO<sub>2</sub>/Si square samples measuring 20 × 20 mm were prepared. The sheet resistance ( $R_\square$ ) of samples was measured using four-probe method. As shown in Fig. 6f, samples with rGO/SAM and Ru SA-rGO diffusion barrier take a decrease in  $R_\square$  of 23.4 and 26% compared to Cu/SiO<sub>2</sub>/Si samples, respectively. The intercalation of rGO/SAM between Cu film and the SiO<sub>2</sub> substrate effectively improves interconnect conductivity, which might be attributed to the reduction of surface scattering and the provision of an additional conductive path<sup>58,59</sup>. Based on this, the support of Ru atoms not only repairs the carbon skeleton of rGO, but also provides free electrons to rGO. This achieves a further enhancement of interconnect conductivity.

To explore the underlying mechanism responsible for the significant increase in Cu interconnect conductivity upon introduction of the Ru SA-rGO/SAM diffusion barrier, we deposited Cu films of varying thicknesses (6.5 nm to 182 nm) on both SiO<sub>2</sub> substrate and Ru SA-rGO/SAM/SiO<sub>2</sub> structure. As verified by AFM in supplementary Figs. 17 and 19, all Cu film thicknesses were precisely measured. For each sample, the resistivity of Cu film was calculated by multiplying the sheet resistance obtained from four-probe method by the corresponding film thickness. The resistivity distribution across different thicknesses for both structures is plotted in Fig. 6g.

Based on the Fuchs-Sondheimer (F-S) model for surface electron scattering resistance and the Mayadas-Shatzkes (M-S) model for grain boundary scattering resistance, the resistivity of thin films can be expressed by the following equation<sup>9</sup>

$$\rho = \rho_0 + \rho_0 \lambda \frac{3(1-p)}{4d} + \rho_0 \lambda \frac{3R}{2D(1-R)} \quad (4)$$

where  $\rho_0$  represents the bulk resistivity,  $\lambda$  is the electron mean free path of the metal,  $d$  is the thickness of the metal film, and  $D$  is the average grain size. The surface scattering parameter  $p$  quantifies electron-surface interactions ( $p = 0$  for completely diffuse scattering and  $p = 1$  for completely specular scattering), and the grain boundary scattering parameter  $R$  characterizes electron-grain boundary interactions ( $R = 0$  for completely transmitting and  $R = 1$  for completely reflecting). Considering all Cu films were deposited under identical conditions (differing solely in deposition time), we may reasonably assume a constant grain boundary reflection parameter  $R_0$  for all samples. Based on this premise and drawing on the material properties of Cu film from reported research<sup>60</sup> ( $\rho_{\text{Cu}} = 1.68 \times 10^{-8} \Omega \text{ m}^{-1}$ ,  $\lambda = 40.0 \text{ nm}$ ,  $D = k_0 d$ ,  $k_0$  is a constant), the equation thereby simplifies to:

$$\rho = \rho_0 + \frac{1}{d} \times \rho_0 \lambda \left[ \frac{3}{4}(1-p) + \frac{3R_0}{2k_0(1-R_0)} \right] \quad (5)$$

Based on the simplified equation, we performed linear fitting of the  $\rho - 1/d$  relationship as shown in Fig. 6h, with the slope and intercept of the fitted curve displayed in supplementary Table 9. While we cannot directly obtain precise  $p$  values from the  $\rho - 1/d$  relationship fitting curves, we can accurately calculate the difference in  $p$  values ( $\Delta p$ ) between the two structures by subtracting the slopes of the two curves:

$$K_1 - K_2 = \frac{3}{4} \rho_0 \lambda (p_2 - p_1) \quad (6)$$

$$\Delta p = p_2 - p_1 = \frac{4(K_1 - K_2)}{3\rho_0\lambda} \quad (7)$$

By substituting the slopes of both curves into the equation, we obtain  $\Delta p = 0.4986$ . This result demonstrates that the introduction of Ru SA-rGO/SAM significantly enhances the transition trend from diffuse to specular electron scattering at the surface, which means the change in surface scattering constitutes a significant contributor to the enhanced conductivity of Cu interconnect.

### Mechanism of Cu diffusion blocking of Ru SA-rGO/SAM

Based on the analysis above, the physical and chemical blocking mechanism of Ru SA-rGO/SAM is illustrated in Fig. 7a. On the one hand, the rGO lattice itself can serve as a physical barrier to block Cu vertical diffusion. In addition, the O-containing functional groups in rGO can also have a certain blocking effect on Cu lateral diffusion. After the Ru-supporting process, the small-sized vacancies are occupied by Ru atoms, thus, preventing Cu diffusion physically. Nevertheless, a reasonable explanation is still lacking for the large-sized vacancies in rGO that are more prone to failure.

On the other hand, Ru SA-rGO/SAM can chemically block Cu diffusion by chemical absorption. To further explore the chemical blocking mechanism of Ru SA-rGO/SAM, a 10-atom model was determined as a typical structure. To simulate the process of Cu diffusion through the vacancy model, we set the state with Cu positioned above the vacancy model as the initial state (IS), and the state with Cu positioned below the vacancy model as the final state (FS). Between IS and FS, 9 intermediate states were set based on the distance between Cu and the plane of the vacancy model, where the state with Cu and the vacancy model being on the same plane is considered the transition state (TS). The optimized structures for the rGO, N-rGO and Ru SA-rGO models in different states are shown in Fig. 7b. It can be observed that Cu is absorbed by forming chemical bonding. The potential barrier ( $E_b$ ) can be defined as  $E_b = \Delta E_{ac} - \Delta E_{ai}$ , where  $\Delta E_{ac}$  and  $\Delta E_{ai}$  represent the adsorption energy of a certain state and IS, respectively. The trend of  $E_b$  changing with the states is shown in Fig. 7c. It can be seen that all three models exhibit lower adsorption energy as Cu approaching, and reach a minimum value at TS. Therefore, a more negative value of  $E_b$  indicates a stronger chemical blocking ability of diffusion barrier. The  $E_b$  value of rGO, N-rGO and Ru SA-rGO vacancy models is -4.06 eV, -5.35 eV and -6.28 eV, respectively. This result elucidates that the N-doping process can enhance the absorption ability to capture Cu, and the subsequent Ru-supporting process can further improve its diffusion barrier properties.

### Discussion

In conclusion, a ~1.4 nm Ru SA-rGO/SAM diffusion barrier is fabricated using a BEOL compatible process. The supporting of Ru requires a N-doping process as a bridge. It is demonstrated that Ru species are supported as individual single atoms. Ru SA-rGO/SAM exhibits excellent adhesion to Cu, and possesses outstanding thermal and electrical diffusion barrier properties. The good adhesion of Ru SA-rGO/SAM layer is confirmed by tape adhesion test and morphological characterization. STEM-EDS mapping and XRD patterns prove that Ru

SA-rGO/SAM remains effective under annealing treatment condition of 600 °C for 30 min. Through electrical tests including the I-V and TDDb measurement, Ru SA-rGO/SAM shows a  $1.33 \times$  critical electric field and a  $24 \times$  TTF<sub>50%</sub> compared to devices without diffusion barrier. Simultaneously, the addition of the Ru SA-rGO/SAM layer can bring about a 26% decrease in  $R_{sq}$ . We further elucidated the diffusion blocking mechanism enhanced by Ru SA through DFT calculation. Ru atoms not only physically block Cu diffusion by filling the vacancies in GO, but also chemically capture Cu atoms by enhanced adsorption. Our work provides an approach for the next-generation diffusion barrier, which benefits for the development of advanced interconnect technology.

### Methods

#### Preparation of SAM/SiO<sub>2</sub>/Si

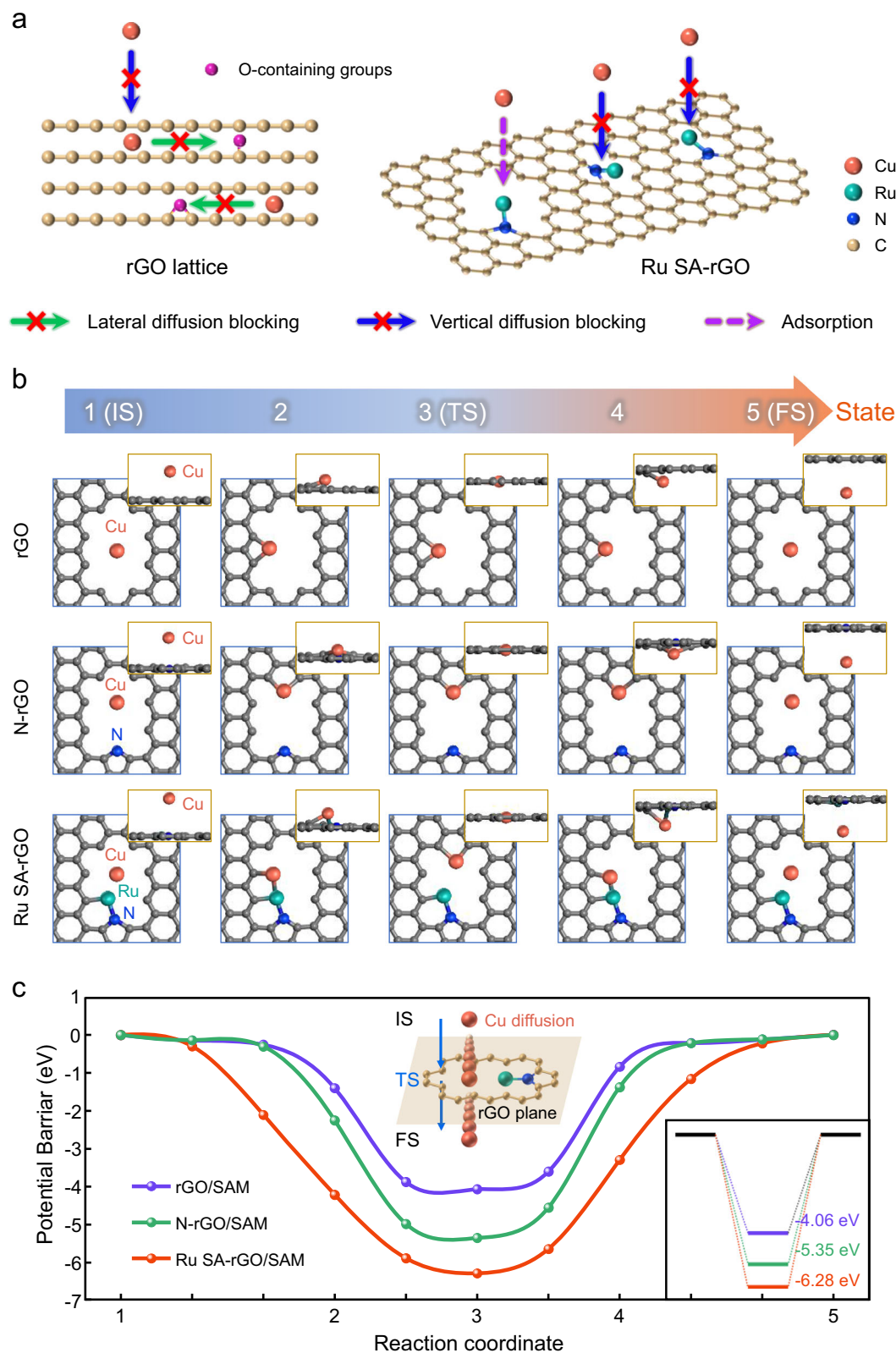
The 20 × 20 mm Si substrates with 40 nm thick thermally oxidized SiO<sub>2</sub> were firstly ultrasonically cleaned in acetone, ethanol, and deionized water for 5 min each, in sequence. Piranha solution was prepared by mixing H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> in a volumetric ratio of 7: 3 with stirring. The cleaned SiO<sub>2</sub>/Si substrates were then immersed in the piranha solution at 90 °C for 30 min to achieve surface hydroxylation. The APTES derived SAM was fabricated by immersion of the surface-hydroxylated SiO<sub>2</sub>/Si substrate into a 5 mM solution of APTES (in a solvent mixture of acetone and water at a 5: 1 ratio) at room temperature for 30 min. Finally, the SAM/SiO<sub>2</sub>/Si samples were rinsed with ethanol and deionized water and dried in an air flow.

#### Preparation of rGO/SAM/SiO<sub>2</sub>/Si

GO was prepared using Hummers method. 0.5 g nano-graphite powder, 0.5 g NaNO<sub>3</sub>, and 40 ml H<sub>2</sub>SO<sub>4</sub> were firstly added into a flask. The mixture was stirred in an ice bath, and 3 g KMnO<sub>4</sub> was slowly added. The system temperature was then raised to 40 °C and reacted for 90 min. Subsequently, 30 ml water was added, and the reaction was continued maintaining constant temperature for another 30 min. Next, 100 ml water was added to prepare crude GO, followed by the addition of 3 ml 30% H<sub>2</sub>O<sub>2</sub> to react with residual oxides. Afterwards, crude GO was centrifuged at 447 g for 2 min to remove the unreacted graphite powder, and then washed four times with deionized water by centrifugation at 7155 g for 15 min per wash cycle. Finally, the washed GO was dissolved in 20 ml water to obtain the GO concentrated solution. 5 ml GO concentrated solution was dispersed in 200 ml water by ultrasonic treatment for 90 min to form GO colloid. Few-layer GO was fabricated on SAM/SiO<sub>2</sub>/Si samples using electrophoretic deposition. The SAM/SiO<sub>2</sub>/Si samples served as anode and a cleaned Cu foil served as cathode in the GO colloid. A voltage of 30 V was applied for 5 min to drive GO micelles to migrate towards the anode surface. The GO micelles adsorbed on the anode surface and underwent a self-limiting reaction with SAM, achieving the deposition of few-layer GO on SAM/SiO<sub>2</sub>/Si samples. The GO/SAM/SiO<sub>2</sub>/Si samples were thermally reduced at 200 °C for 2 h in an Ar atmosphere to prepare rGO/SAM/SiO<sub>2</sub>/Si samples.

#### Preparation of N-rGO/SAM/SiO<sub>2</sub>/Si and Ru SA-rGO/SAM/SiO<sub>2</sub>/Si

During ultrasonic treatment of the GO concentrated solution, N-GO colloid was formed with an extra addition of 250 μl aniline. The remaining steps for the preparation of N-rGO/SAM/SiO<sub>2</sub>/Si samples are consistent with those for rGO/SAM/SiO<sub>2</sub>/Si samples. Through the final thermal treatment, N species from the stacked aniline were incorporated into the carbon skeleton of GO. To synthesize Ru SA-rGO, after the deposition of few-layer N-GO on SAM, the SAM/SiO<sub>2</sub>/Si samples were immersed into a solution containing 1 mM RuCl<sub>3</sub> in water at pH = 1 (adjusted by HCl) for 4 h at room temperature. In the process, Ru species were coordinated with the -NH<sub>2</sub> of aniline in N-GO. The samples were then rinsed by ethanol and deionized water to remove unsupported Ru. The subsequent steps for the preparation



**Fig. 7 | Exploration of the mechanism of single atom Ru-supported (Ru SA)-rGO in blocking Cu diffusion.** **a** Comprehensive mechanism of Ru SA-rGO in blocking Cu diffusion. **b** The optimized structures (the blue chart represents the top view, and the yellow chart represents the side view) and **c** the calculated potential barrier

profile of rGO, N-rGO, and Ru SA-rGO vacancy models in different states (The schematic diagram near the curves illustrates the process of the state changes during Cu diffusion). Source data are provided as a Source Data file.



of Ru SA-rGO/SAM/SiO<sub>2</sub>/Si samples are consistent with those for rGO/SAM/SiO<sub>2</sub>/Si samples. The N-doping process facilitated the anchoring of Ru atoms into GO.

### Instrument of characterization and tests

The morphology of samples was characterized using SEM (MIRA3, TESCAN) analysis and TEM (Talos F200X G2, Thermo Scientific) analysis. HAADF-STEM was conducted on a system equipped with spherical aberration corrector and operated at 80 kV. Raman spectra were acquired through confocal microscopic Raman spectrometer (Renishaw inVia Qontor). XPS spectra were carried out to analyze the chemical composition of samples by Thermo Fisher Scientific ESCALAB-250Xi with an Al K $\alpha$  radiation source. Prior to XPS analysis, the samples were ultrasonically cleaned sequentially in ethanol and deionized water to remove surface contaminants. After cleaning and drying, the samples were rapidly transferred to the XPS chamber to minimize air exposure. The details of and parameters used for XPS spectra fitting are shown in supplementary Table 13. The thickness and roughness of samples were measured by AFM (FastScan, Bruker). For thickness measurement, an adhesive tape was applied to protect a designated area on the SiO<sub>2</sub> substrate. Following the sequential deposition of SAM, rGO, and supporting of Ru, the tape was removed prior to annealing to create the thickness step. XRD patterns were collected to determine the phase structures of the samples by Mini Flex 600 with a Cu K $\alpha$  radiation source in a condition of 40 kV, 15 mA at a scan rate of 5° min<sup>-1</sup>. The sheet resistance was measured by four-point probe station (ST2258C, Suzhou Jingge). I-V measurement and TDDb measurement was tested through Kethley 4200 to evaluate the electrical properties of devices.

### DFT structural optimization and calculations

All the computations were performed by the density functional theory (DFT) method with projector augmented wave (PAW) pseudo-potentials using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) in the Vienna Ab initio Simulation (VASP 5.4.4)<sup>61–63</sup>. The plane wave cutoff energy was set as 450 eV. The energy and force convergence threshold were adopted 10<sup>-5</sup> eV and 0.05 eV Å<sup>-1</sup> for structural optimizations. The Brillouin zone was sampled by 2 × 2 × 1 *k*-points using the Monkhorst–Pack scheme. The van der Waals interaction between atoms was treated using the DFT-D3 method with Becke-Jonson damping<sup>64</sup>. A vacuum of 27 Å along the *z*-direction was fixed to avoid interaction between adjacent layers. Solvation effects were taken into account with the VASPsol model using the dielectric constant of water at 78.5<sup>65</sup>. The climbing image nudged elastic band (CI-NEB) method is used to calculate the migration energy of Cu atom diffusing in rGO, N-rGO, and Ru SA-rGO vacancy models<sup>66</sup>.

### Statistics and Reproducibility

Data in Figs. 2b–e, h–j, 4d–e, 5b–f are representative of three independent experiments with similar results. Data in Fig. 4b, c are representative of four independent experiments with similar results. Data in Fig. 2k are representative of five independent experiments with similar results.

### Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

### Data availability

The data that support the findings of this study are available in the supplementary material of this article. Additional information is available from the authors on request. Source data are provided with this paper.

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## Competing interests

The authors declare no competing interests.

## Additional information

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