Formation and Conductance of Cd and Ti Single-Atom Contacts at Room Temperature*

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Break junctions of some HCP metals are known to yield single-atom contacts (SACs) frequently at 4 K but rarely at room temperature (RT). In this work, we show that SACs of Cd and Ti can be produced at RT not by opening their junctions but by closing them. For both Cd and Ti, the conductance histogram measured at junction closing reveals a clear SAC peak whereas the SAC peak appears marginal in the histogram obtained at junction opening. Because SACs are formed through necking deformations in the junction opening, while not in the junction closing, our observations suggest that the rare SAC formation reported for some HCP break junctions at RT would be due to necking deformations. The observed histograms also determine the hitherto unknown SAC conductance of Cd and Ti as $0.7G_0$ and $0.8G_0$, respectively.

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I. INTRODUCTION

Single-atom contacts (SACs) of metals are the smallest of all metal contacts and exhibit a variety of mechanical and electronic properties that cannot be observed on macroscopic contacts [1]. Electron transport through an SAC, for example, becomes ballistic and shows a conductance τG_0 , where τ is the electron transmission probability and $G_0 \equiv 2e^2/h$ is the quantum unit of conductance. In many experiments, SACs are produced by the so-called break-junction method where a pair of macroscopic metal electrodes are first brought into contact and then separated apart. The contact point is stretched and reduced in size by successive necking deformations. The neck occasionally shrinks to an SAC just before the junction completely breaks off. It can then be naturally anticipated that SACs should be formed more easily at room temperature (RT) than at cryogenic temperatures where metals become hard and less deformable. In previous break-junction experiments, this temperature dependence of metal plasticity has not, however, been an importance issue because most experiments were made on such metals as Au, Cu and Al. Necking deformations of these soft FCC metals depend weakly on temperature and can produce SACs equally well at RT and at 4 K.

On the other hand, temperature affects the SAC formation of non-FCC metals. In opposite to the temperature dependence of metal plasticity, however, SACs of non-FCC metals seem to be formed more frequently at low temperatures than at RT. Smit *et al.* [2], for example, report that breaking of Mg junctions at 4 K produces a sharp SAC peak at $1G_0$ in the conductance histogram whereas the histogram measured at RT exhibits no peaks

below $4G_0$. Similar results have been obtained on junctions of Ga [3], Zn,[4, 5], and Co [6–9]. The conductance histogram of these metals shows the SAC peak at 4 K or below but not at RT. This SAC peak missing has been discussed separately for each metal, but we consider it a general phenomenon commonly observed for break junctions of non-FCC metals, in particular for those of HCP metals. As we shall discuss later in Sec. IV, there are a few mechanisms that can lead to the SAC peak missing. Among those mechanisms, we consider that deformations of HCP metals would likely be the dominant one. Presumably, necking deformations of most HCP junctions would be curtailed by premature fracture and cannot produce SACs at RT. The importance of junction deformation on the SAC formation has been invoked for explaining the missing SAC peak of Ga [3] and also indicated in our previous experiment [10] where we measured the conductance of Mg alloys of high ductility and found a couple of low conductance peaks that are missing for ordinary Mg.

The relevance of the necking deformation in the SAC formation can be readily tested by carrying out those junction experiments that involve no necking deformations. If the deformation really matters, a clear SAC peak could be observed in such deformation-free experiments. There are various non-mechanical techniques that can fabricate metal SACs, e.g. electron-beam thinning [11, 12], electromigrated break-junction method [13, 14] and contact formation by electrodeposition [15] and fast ionic migration [16]. In this work, we adopted a simple method of electrode touching, i.e. junction closing. After touching, electrodes undergo compressive deformations [17] but they remain deformation-free until the first moment of touching. Electrode touching often accompanies a discontinuous jump in conductance known as a “jump to contact” and some experimental studies have been made on this phenomenon [18, 19]. These experiments were, however, conducted at low temperatures and cover no HCP metals. In our experiment, we measured the conductance of Cd and Ti junctions at RT not only during the junction opening but also at the junction closing. Two conductance histograms thus obtained, the junction-opening

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FIG. 1: Typical conductance traces observed at junction opening (a) and closing (b) of a Cd junction. The zero of the displacement is chosen arbitrarily.

and the junction-closing histograms, are compared to examine the appearance (or absence) of the SAC peak in these histograms.

II. EXPERIMENT

The experimental setup and measurement procedures are mostly the same as those used in our previous experiment on Mg alloys [10]. Our electrodes are a pair of short pieces of wire, the diameter and purity of which are 1 mm and 99.999% for Cd and 1 mm and 99.99% for Ti, respectively. Two wire pieces are arranged to form a cross junction, and the wire-wire distance is controlled by a tubular piezo scanner (used as a uniaxial translator) and a piezo motor. Temporal variation of the junction conductance (referred to as the conductance trace) was measured under an applied bias of 100 mV. Conductance traces are acquired during both opening and closing a junction. The junction opening/closing speed is 36.5 nm/s, but measurements with higher speeds up to 731 nm/s were also conducted. All measurements were made at RT in a ultrahigh vacuum $\sim 2 \times 10^{-8}$ Pa.

III. RESULTS

A. Cd

Figures 1(a) and (b) show typical conductance traces observed at opening and closing a Cd junction, respectively. At junction opening, the trace exhibits plateaus at $1.5G_0$ and $0.9G_0$, whereas at the junction closing, the conductance jumps up and shows a long plateau at $0.8G_0$. In Fig. 1(b), the plateau extends longer than 0.1 nm and similar long plateaus were found in other junction-closing traces. Such long plateaus are unexpected at junction closing where a contact becomes squashed instead of being stretched. Simulations of Au junctions [19] indicate that the electrode distance discontinuously decreases by approximately 0.1 nm at the jump to contact. This implies that junction atoms after the jump to contact would be slightly loose-packed. Similarly for Cd, their junctions after the conductance jump would become a little squeezable.

FIG. 2: Junction-opening (green) and junction-closing (red) histograms of Cd obtained at RT.

We carried out measurements on three different specimens and acquired 3,750 and 1,350 conductance traces at junction opening and closing, respectively. Conductance histograms constructed from these traces are compared in Fig. 2. Because different numbers of traces are used for each histogram, the histogram for one specimen is first normalized by the total number of traces used for that histogram. Three normalized histograms obtained on three specimens were then summed up to produce the histogram shown in Fig. 2. In the junction-opening histogram, the first peak appears at $0.74G_0$ with a larger second peak at $1.5G_0$. The histogram also reveals a small structure around $2.7G_0$ and shows an appreciable intensity above $3G_0$. On the other hand, the junction-closing histogram only exhibits a large single peak at $0.73G_0$ and nothing else. This peak appears slightly off-positioned from the $0.74G_0$ peak in the junction-opening histogram but they should certainly be the same peak (referred to as the $0.7G_0$ peak). This peak, however, shows different intensity in two histograms and appears more pronounced in the junction-closing histogram than in the junction-opening histogram.

No data have been reported on the SAC conductance of Cd so that we have at this time no firm evidence that the $0.7G_0$ peak is the SAC peak of Cd. The peak position, however, agrees with that of the SAC peak of Zn which lies $(0.7 - 0.9)G_0$ [4]. Because Cd and Zn are in the same column of the periodic table and have the same valence electron configuration, they should show similar SAC conductance [20]. The observed $0.7G_0$ peak is thus likely the SAC peak of Cd. In the case of Zn, the SAC peak is found to consist of two closely separated subpeaks [4]. No such splitting, however, can be recognized on the $0.73G_0$ though the peak appears rather broad compared to the sharp SAC peak of Au.

In experiments at RT, possible effects of residual gases, hydrogen in particular, are unavoidable even in ultrahigh vacuum, and there remains a possibility that the $0.7G_0$ peak of Cd might be a gas-induced SAC peak. A reasonable check for this gas effect would be to carry out measurements in hydrogen-free environment at 4 K. We tried mechanically controllable break-junction (MCBJ) experiment on Cd but found out that Cd wires are too soft to make reliable MCBJ specimens. Measurements of the SAC conductance of Cd at 4 K are thus yet uncompleted.

Concerning other conductance peaks in the histograms, the $1.5G_0$ peak appearing in the junction-opening histogram reasonably agrees with the second peak of Zn

FIG. 3: Junction-opening (green) and junction-closing (red) histograms of Ti obtained at RT.

which locates at $1.4G_0$ [4]. Similarly, the small feature at $2.7G_0$ consistently corresponds to the Zn third peak at $2.5G_0$, though this Zn peak appears not as a small structure but as a large peak. For Zn at 1.5 K, Scheer *et al.* [4] obtained both the junction-opening and the junction-closing histograms and found no essential differences between their profiles and peak structures. Their results are in marked contrast to our histograms shown in Fig. 2 where two histograms are dissimilar and exhibit different features, especially for the SAC peak. In spite of some agreements in peak positions, the histograms of Zn at 1.5 K and those of Cd at RT manifest different characteristics.

B. Ti

Figure 3 compares the junction-opening and the junction-closing histograms obtained for Ti at RT. We carried out measurements on two Ti specimens and acquired 2,000 and 5,600 traces on each of them, respectively. In Fig. 3, we show the histograms constructed from 3,000 traces (2,250 junction-opening and 750 junction-closing traces, respectively) which consist of the latter half of the 5,600 traces obtained on one specimen. As in the case of Cd, two histograms are again dissimilar and exhibit different peak structures. In the junction-opening histogram, a peak appears at $1.5G_0$ with a small structure around $0.8G_0$. The junction-closing histogram, on the other hand, shows a large single peak at $0.8G_0$. The $0.8G_0$ peak can also be observed in some partial histograms obtained on another specimen but in its total histogram, the peak structure becomes obscured compared to that shown in Fig. 3.

Because the traces used for the histograms in Fig. 3 were acquired during the latter half of the measuring hours, junction contaminations should be seriously considered particularly for Ti which is highly reactive to residual gases. To examine the possible effects of gas adsorption, we carried out MCBJ experiments on Ti at 4 K. Figure 4 shows the resulting junction-opening histogram constructed from $\sim 4,000$ traces. The histogram clearly shows the first peak at $0.86G_0$ and the second peak at $\sim 2G_0$. The first peak reveals a shoulder and might consist of two subpeaks at $\sim 0.7G_0$ and $1G_0$, respectively. Though this fine feature cannot be resolved for the $0.8G_0$ peak shown in Fig. 3, the $0.8G_0$ peak and the first peak in Fig. 4 should be the same peak and likely to represent the SAC peak of Ti. As for Cd, the SAC peak of Ti appears

FIG. 4: Junction-opening histograms of Ti obtained at 4 K.

more pronounced in the junction-closing histogram than in the junction-opening histogram.

No SAC conductance data, theoretical or experimental, have yet been reported for Ti and as in the case with Cd, no direct comparison can be made at this time on the observed SAC conductance of Ti. Our preliminary MCBJ measurements [21] on Zr and Hf show no peaks in their junction-opening histograms at RT but one experiment made on Hf at 4 K found a peak around $0.8G_0$, similar to the one shown in Fig. 4. Because Ti and Hf occupy the same column in the periodic table, this result on Hf suggests that $0.8G_0$ would be a reasonable estimate for the SAC conductance of Ti. On the other hand, other 3d transition metals such as V, Fe, Co, and Ni all show their SAC conductance around $(1.5 - 2)G_0$ [22, 23]. Compared to these values, the Ti SAC conductance of $0.8G_0$ appears relatively low. The low SAC conductance might be partly due to the smaller number of 3d electrons (two for Ti), but the SAC conductance of V, which has three 3d electrons, amounts to $1.8G_0$ [22]. Though there is no linear correlation between the SAC conductance and the number of 3d electrons, the seemingly low SAC conductance of Ti appears exceptional and calls for further investigations.

IV. DISCUSSION

Our results shown in Figs. 2 and 3 clearly indicate that, for both Cd and Ti, the junction-opening and the junction-closing histograms are dissimilar and exhibit different peak features. In particular, the SAC peak appears more pronounced in the junction-closing histogram than in the junction-opening histogram. As we mentioned in Sec. I, SACs are produced through necking deformations in the junction opening while they are formed by touching electrodes in the junction closing. The clear SAC peak in the junction-closing histogram thus provides a supportive evidence for our assumption that necking deformations might be responsible for the reduced SAC peak in the junction-opening histograms of some HCP metals at RT. However, before jumping to a conclusion, we have to examine other possible mechanisms that can lead to the SAC peak missing.

When the conductance histogram of break junctions shows no SAC peak, there would be three possible sources for the peak missing; instability of SAC, broadening of the SAC peak, and suppression of the SAC formation. We take up these mechanisms one by one and first discuss the SAC instability at RT. The stabilization energy W of an SAC can be expressed [24] as $W = W_0 - \alpha V - \beta F$

where V and F are the bias and the tensile force acting on an SAC, respectively, W_0 is the energy at $V = 0$ and $F = 0$, and α and β are positive coefficients. An SAC becomes unstable when W_0 is small or V and/or F are large. Smallness of W_0 is not a trivial issue for such metals as Cd which has a low cohesive energy (1.16 eV/atom) that amounts to less than 40% of that of Au. The junction-closing histogram in Fig. 2, however, shows the clear SAC peak and hence ensures sufficient stability of Cd SACs to be observed at RT. Because other HCP metals have higher cohesive energies, thermal instability of their SACs at RT would also be unlikely. Similarly, the high-bias instability cannot explain the observed difference between the junction-opening and the junction-closing histograms because both histograms were measured under the same bias.

On the other hand, the influence of F needs some considerations because F changes sign and tends to destabilize and stabilize SACs in the junction opening and the junction closing, respectively. In fact, it has been experimentally verified that the self breaking of junctions made under $F = 0$ yields SACs of longer lifetime [25]. As to the conductance histogram, however, no clear evidence has yet been reported on the influence of F . Because the decrease/increase of W by the positive/negative F does not depend on metal species, it should work for all metals and becomes more enhanced at lower temperatures due to the Boltzmann factor. For archetypal FCC metals, however, no substantial differences have been observed between their junction-opening and the junction-closing histograms at low temperatures, and it is even the case for Zn [4] as we mentioned before. We therefore consider that the negative F might help stabilize Cd and Ti SACs during the junction closing but the influence of F would not be so strong to account for the large difference in the SAC peak seen in Figs. 2 and 3.

In relation to the influence of F , we note that our junction opening/closing speed is much faster than that used in MCBJ experiments. Faster speed yields larger F [25] and may tend to suppress the SAC peak in the junction-opening histogram. Though no results of MCBJ experiments have been made on Cd and Ti at RT, our MCBJ experiments at RT on Co [9], Hf, and Zr [21] found no SAC peak in their junction-opening histograms. This result shows, though indirectly, that the fast opening/closing speed may be irrelevant to the reduced SAC peak of Cd and Ti in their junction-opening histograms.

The broadening of the SAC peak often occurs for transition metals because the transmission of d -conductance channels of these metals sensitively varies with a contact geometry. Fluctuations of the SAC geometry at RT then lead to the broadening of the SAC peak and sometimes entirely flatten the peak. We consider that the absence of the SAC peak in the histogram of Ni at RT would be due to this peak flattening [9]. Though such peak broadening might explain the SAC peak missing for Ti, the mechanism does not work for SACs of sp metals like Cd and Zn where the transmission through a major transparent channel little varies with the contact geometry [2, 26].

We come back to our assumption on the relevance of necking deformations to the SAC formation. When a junction breaks, it follows a variety of deformation pathways. Some of them reach to SACs while others end up

with fracture. As we mentioned in Sec. I, we consider that for HCP junctions at RT, most of their necking deformations would be terminated by premature fracture. This would reduce the chance of SAC formation and suppress the SAC peak in the junction opening histogram. Though this assumption accounts for the observed difference between the junction opening and the junction closing histograms, it is yet unclear what kind of deformation processes lead to this fracture and why it occurs predominantly at RT. Our molecular dynamics simulations of the stretching of Mg nanowires [27] show that some Mg nanowires tend to fail after forming a long icosahedral nanowire. These icosahedral nanowires are abundantly formed in simulations at RT but rarely observed at 4 K. The rupture of icosahedral nanowires would thus be a possible candidate of the premature fracture. Unfortunately, we have little information on the conductance and other properties of icosahedral nanowires and cannot conclude at this time whether the fracture of Cd and Ti is actually made through the formation of such icosahedral nanowires. Simulation of the conductance histogram of HCP metals at RT, similar to the one [28] carried out for FCC metals at 0 K, should be needed for clarifying this issue.

It should be finally noted that our junction-closing histograms of Cd and Ti both exhibit the SAC peak but no other peaks. This is in contrast to the junction-closing histogram of Zn [4] measured at 1.5 K where multiple peaks are observed. In our experiment, many conductance traces measured in the junction closing make a sudden jump-up to high conductances. Even in such cases as shown in Fig. 1(b) where the trace shows the first plateau, it rarely exhibits higher-conductance plateaus. This leads to the single-peaks structure of the junction-closing histograms shown in Figs. 2 and 3. We consider that, in the junction closing, the compressive deformation of the electrodes rapidly increases the contact area and effectively crashes the higher-conductance plateaus. At RT, the junction electrodes after the tensile fracture are likely to make some structural relaxations and take a blunt geometry. In the subsequent pressing of these blunt electrodes, their contact area would naturally grow up very rapidly. At 1.5 K, on the other hand, the fractured electrodes would mostly retain their elongated geometry, and then the junction closing gradually thickens the contact, a reversal of the contact thinning by necking deformations. This might explain why the junction-closing histogram of Zn at 1.5 K exhibits the same multiple peak structure as that of its junction-opening histogram. These are, however, speculations, and the full explanation requires molecular-dynamics simulations and/or direct electron-microscopy observations of closing junctions.

V. SUMMARY

We have measured the conductance of Cd and Ti break junctions at RT and separately constructed the junction-opening and the junction-closing conductance histograms. For both Cd and Ti, these two histograms are dissimilar and exhibit different peak structures. A pronounced SAC peak appears in the junction-closing histogram but the peak becomes marginal in the junction-opening his-

togram. The clear observation of the SAC peak in the junction-closing histogram suggests that, for junctions of Cd, Ti and probably for other HCP metals, necking deformations, which are present in the junction opening but

absent in the junction closing, would promote premature junction fractures at RT and lead to the vanishing SAC peak in the junction-opening histogram.

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