RESEARCH ARTICLE

Effect of roughness on the conductivity of vacuum coated flexible paper electrodes

Gaurav Rawal1 • Animangsu Ghatak1,2
1 Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh, India
2 Center for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh, India

Correspondence
Gaurav Rawal, Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh, India.
Email: drgaurav@iitk.ac.in
Animangsu Ghatak, Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India.
Email: aghatak@iitk.ac.in

Funding information
Department of Science and Technology, Grant/Award Number: SB/SC/CE/036/2013

Abstract
Flexible conducting materials are required for the design and fabrication of a host of applications involving flexible electronic items. A flexible substrate like paper or polymer is generally employed for deposition of metal by a variety of processes. Among many physical properties, the roughness of the substrate is considered an important parameter, although, its exact role on effective conductivity of the coating is not known. Nor any study has been carried out to understand how the three-dimensional porous structure of the substrate surface affects the microscopic packing of grains that constitute the metal coating. With the objective of elucidating the effect of substrate roughness on the conductivity of paper electrodes, we have used six different commonly available papers for vacuum coating with copper. For a smooth substrate, the grains that constitute the coating appear spherical, however, turns ellipsoidal as the substrate roughness and heterogeneity is increased; ellipsoidal grains result in higher packing efficiency leading to higher conductivity. We have also presented a model to relate the packing efficiency to the asphericity, polydispersity, and skewness of size distribution of grains.

KEYWORDS
ellipsoid, paper electronics, physical vapor deposition, polydispersity

1 INTRODUCTION

Flexible substrates of different kind, for example, polymeric membrane[1,2] crosslinked elastomer[2,3] paper,[4–10] fabrics of a different kind[11–13] have been used for making flexible, electrically conducting sheets, essential for a large number of scientific, and engineering applications. Among these many different substrates, paper is considered to be an attractive option because of its many useful properties. For example, paper is ubiquitous; the technology for making different kinds of paper and that for writing or printing on it is well established; paper is porous and therefore allow the ink material to percolate through it thereby bonding strongly with it easily; paper can be easily disposed of and so on. Several different methods can be used for depositing a conductive coating on paper, for example, solution processing[11,13] thermal evaporation[9,14] electro-deposition, in-situ deposition of metal nanoparticles[15] and nano-wires,[16] ink-based coating and printing,[16–19] physical vapor deposition...
TABLE 1 Different types of substrates used for coating: Their make, surface roughness, and surface energy

| S. No. | Name of substrate | Make/Manufacturing company | Surface energy [mN/m] | Surface Roughness [200 µm Scale] |
|--------|------------------|----------------------------|-----------------------|----------------------------------|
| 1      | Trace paper      | Desmat Tracing Paper HC27 (90 µm thick) A4 | 27.3 ± 0.83          | 1.66 ± 0.76 µm                   |
| 2      | Printing paper   | JK Copier Paper - A4, 75 GSM         | 46.6 ± 4.3           | 1.81 ± 0.39 µm                   |
| 3      | Drawing sheet    | DI-KRAFT Coloured Drawing Sheet150GSM| 24.41 ± 3.22         | 2.56 ± 0.55 µm                   |
| 4      | Sparkly paper    | Pindia, Printed Glitter Sheet Holographic Papers 250 GSM | 33.83 ± 6.5          | 4.69 ± 1.8 µm                    |
| 5      | Circular patterned paper | KIDSTAB Ziggle A4 Size Thick Pattern Design Printed Papers 300 GSM | 27.4 ± 0.6           | 1.86 ± 0.82 µm                   |
| 6      | Silicon wafer    | DS Scientific & Nano Technology (P type Boron, 430 µm thick) | 35.19 ± 0.13         | 1.1 ± 0.12 nm                    |

(PVD)[20–22] and vacuum filtration.[23] Over the past decade paper-based conductors have been widely used in various technological applications such as circuits,[24] electrical shielding,[25] electromagnetic shielding,[26] chemical sensor,[27,28] and electrochemical sensor.[29] There are several paper substrates available, with wide variation in topographical and surface chemical heterogeneity. Despite, paper being increasingly used in making flexible electronic devices, it is not known which specific characteristics of the paper are important and what are their optimum values that are expected to result in an ideal flexible conductor. Even the surface of a specific kind of paper varies spatially and randomly in regard to its hierarchical roughness and surface energy, both of which are expected to affect the integrity of the conductive coating.

In this report, we have examined six different commercially available papers to show that for vacuum coated thermally evaporated copper coating, the electrical resistance decreases with increase in roughness of the substrate; surface having the largest root mean square roughness results in minimum resistance. In general, the roughness of the substrate is thought to increase the effective path length of electrons, thereby increasing the electrical resistance. However, results presented here show that resistance of the coating is a function of its micro-structure that varies with the topographical heterogeneity of the surface. The vapor of copper condenses on the substrate via nucleation of grains, the shape and size of which depend on the surface heterogeneity. On a rough surface, the grains tend to be elongated and ellipsoidal rather than being spherical for a smooth substrate; their packing efficiency too becomes different. For a substrate consisting of sharp topographical features, the integrity of the coating diminishes because of the effect of the large curvature at these locations, resulting in increase in the resistance. For a perfectly smooth substrate, the occurrence of spherical grains decreases the packing efficiency, thereby diminishing the integrity of the coating with the consequent increase in resistance. We have also developed a model relating statistical characteristics of the packing of grains to identify substrates, which are expected to result in minimum resistance.

2 | MATERIALS AND METHODS

Papers of different types: Trace paper, Printing paper, Drawing sheet, Sparkly paper, Circular patterned were procured from the local market and were used as acquired without any treatment (Table 1). Silicon wafer (P-Type Boron 4 inch, 430 µm thick) purchased from DS Scientific & Nano Technology was used as a reference substrate. Copper foil of thickness 0.1 mm, obtained from Lobachemie, was used for coating purposes. A high vacuum coating unit (Hind High vacuum Co. (P) Ltd., Model: 12A4D) was used for thermal evaporation and deposition of copper on the substrate.

3 | RESULTS AND DISCUSSIONS

3.1 | Surface roughness and surface energy of substrates

Five different commercially available paper and silicon wafer were used as substrates for coating by thermal evaporation of copper. Table 1 presents the surface roughness and surface energy values measured for these substrates. The surface roughness values were measured using contact mode profilometry with scan size 200 µm x 200 µm and 500 µm x 500 µm. The roughness values of these substrate were also measured using AFM at 500 nm x 500 nm, 5 µm x 5 µm and 10 µm x 10 µm length scales. The Printing and Drawing papers were porous, whereas the Trace paper was rough but non-porous. The Trace paper, Printing paper and Circular patterned paper substrates showed similar surface
3.2 Effect of substrate on the resistance of the coated paper

Figure 1A shows the schematic of the experiment in which the substrate, a flat sheet of paper was placed above a tungsten coil inside the closed chamber of a vacuum coating unit. The desired quantity of copper (Cu) placed inside a tungsten coil was heated inside the chamber, maintained at $10^{-5}$ bar pressure. The exposure time and current were maintained at 30 seconds and 60 amp, respectively. Cu evaporated inside the coil, diffused out of it and then condensed on a substrate positioned vertically above the coil. Figure 1B depicts the optical image of a typical Cu-coated Trace paper (A4 size). The thickness of the copper coating as a function of radial distance (represented as $\square$ Figure S3(c)) from the center of the trace paper was measured by Contact Mode Profilometry (figure S3(c, d)) (Bruker Dektak XTL). At the center of the paper, vertically above the position of the coil, the thickness was maximum; it decreased radially away because of the increase in diffusion length of the vaporized metal from the coil (Figure 1C). Therefore, small samples of radius $4 \text{ cm}$ were cut out from the central portion of the coated paper for conductivity measurement, where the spatial variation in conductivity was expected to be limited. The electrical resistance of the copper layer on different substrates was measured roughness values for $5 \mu m \times 5 \mu m$ and $200 \mu m \times 200 \mu m$ length scales but the surface roughness of patterned paper was different from the other two for the scan area $500 \mu m \times 500 \mu m$.

The surface energy values were measured using Owens and Wendt model\textsuperscript{[30]} with water and pentadecane as the liquids with known values of dispersive and polar components of surface energy. Pentadecane was found to completely wet the surface of all papers as mentioned in the supplementary material. These liquids penetrated the surface of only the printing paper. The surface roughness values could affect the measurement of contact angle of these liquids; therefore, the surface energy values that we estimated was in essence an effective surface energy, which gives an idea of interaction of the substrate with the copper layer deposited on it. The bonding of the copper coating with the substrate is expected to be stronger for larger surface energy of the substrate. In Table 1, we present the detail characteristics of these different substrates.

Surface energy values were estimated using Owens and Wendt\textsuperscript{[30,31]} model (figure S13) and the surface roughness was measured using Contact mode profilometry with scan size $200 \mu m \times 200 \mu m$. The error values in each case represent the standard deviation of data from five measurements.
via two different methods: by using a multimeter (Figure S1(b)) and by obtaining the Electrochemical Impedance (Autolab PGSTAT302N) (Figure $S_1$). The resistance of copper coated paper $R$ increased with increase in length of the coated paper ($L$). However, the resistance did not decrease to zero, for $L \to 0$ (Figure 1C, $S_1$). The finite value of $R_{L \to 0}$ signified the presence of contact-resistance of the wire and imperfect contact with the multimeter tips. In order to diminish any inconsistency due to this inaccuracy in the measurement, the resistance per unit length (RPL) was calculated by obtaining the slope of the $R$ vs $L$ curve. In subsequent analysis, $\Delta R/\Delta L$ was used as the measured parameter. For all substrates, the impedance of the copper coating (figure $S_1(c)$) was found to be independent of the frequency with zero phase angle, implying that the coating was a pure resistor, and its resistance varied linearly with length. The bar chart in Figure 1D shows that for most substrates, the surface roughness varied by over an order of magnitude. Furthermore, the RPL values followed the same trend for both measurement methods, but there was some disparity between them. Measurement of resistance using multimeter was a step process with the steps increasing by 1 cm length, whereas, for impedance spectroscopy, the measurement was done for a single strip of length 5 cm. In both these measurement methods, the values get affected by the contact resistance; however, since for multimeter, measurement of resistance is done using steps of smaller lengths, the RPL values calculated using this method were expected to be more accurate. Therefore, in subsequent analysis, the RPL values from multi-meter measurement were used. Figure 1E shows the variation of RPL with surface energy and surface roughness. RPL of the substrate increases with an increase in the surface energy (Figure 1E1) of the substrate, albeit with some exceptions. The data presented in Figure 1(E1) shows that for most papers, the surface energy of the substrate lies between 28–32 mJ m$^{-2}$, except for printing paper (Xerox paper), for which the surface energy was 46 mJ m$^{-2}$. The printing paper with maximum surface energy among all the substrates showed a modest RPL of 0.2 ohms cm$^{-1}$. The roughness, $\Delta$ of these surfaces were measured at two different length scales: 200μm x 200μm (represented as $\Delta_{200μm}$) using Contact mode profilometry (Bruker Dektak XTL) (Figure 1(E2)) and at 5μm x 5μm (represented as $\Delta_{5μm}$) by using Atomic Force Microscopy (Bruker MultiMode 8) (Figure 1(E3)). RPL of the coated substrates was found to increase with increase in the surface roughness $\Delta_{200μm}$ of most substrates except that for silicon wafer (Figure 1(E2)). Despite being atomically smooth with $\Delta$ much smaller than that of the Trace paper, Silicon wafer showed ten times higher value of RPL than the Trace paper. Figure 1(E3) demonstrates that the RPL of the coated substrates decreased with an increase in surface roughness $\Delta_{5μm}$.

Scanning Electron Microscopy (SEM) (SUPRA 40 VP and CARL ZEISS EVO 50) images of different coated and uncoated papers presented in Figure 2(A-H), show that the copper coating was not a uniform and continuous film but consisted of closely packed grains of different shapes and sizes Figure 2E-H. It is worth pointing out that in 2 μm x 2 μm SEM scan of the patterned paper (Figure 2E), it appeared smooth or featureless as compared to other substrates as the roughness features of it had length scales larger than than the scan size. However, the SEM and AFM images of the patterned papers at larger length scales: 2 μm x 2 μm, 5 μm x 5 μm and 200 μm x 200 μm, as presented in figure S2(e and V) and S2(q), show that roughness features do appear as sharp corners. Figure 2E-H, S2 shows that the nature of the packing varied with substrates; it was closely packed for the Trace paper, but consisted of cracks at sharp corners and wavy edges that decorated the topography of different other papers (Sparkle and Patterned paper, figure S2(p,q)). Importantly, the cracks were also found for coating on the atomically smooth surface of the silicon wafer (Figure 2H, S2(r)). Whereas for the paper substrates, the cracks appeared due to large curvature, for the Silicon wafer, it appeared due to heteroepitaxy$^{[32]}$. Presence of cracks within the coating expectedly resulted in large RPL values. The SEM images in Figure 2 also show that the constituent grains for both silicon wafer and patterned paper were spheroidal (Figure 2G, H), whereas for the trace paper the grains were ellipsoidal (figure 2E). The shape and size of the grains deposited on the substrates depend on surface heterogeneities. For example, surface with low surface roughness leads to formation of homogeneous uniform microstructure with inhibited grain growth and for coarser surfaces pinning of the grains lead to asymmetric grain growth.$^{[34–35]}$

Since the packing efficiency is expected to increase from spheroidal to ellipsoidal grains, the packing of grains for Trace paper was less susceptible to crack formation than the silicon wafer and the patterned paper. Nevertheless, the grains for a particular substrate were not of uniform size and shape, and the distribution in size and asphericity of grains on different substrates was different. To capture the difference in statistical features of coating on different substrates, the length of major and minor axes ($a$ and $b$ respectively) of grains were obtained, and their size and asphericity or aspect ratio (irrespective of the orientation of grain) were estimated as $r = \sqrt{ab}$ and $l = b/a$ respectively.

In order to encapsulate the grains to measure the size and asphericity the contrast of the image was increased as shown in Figure 2E. For each case, a large number of
FIGURE 2 (A-D) SEM images represent different substrates used in experiments. (E-H) SEM images represent copper coating on these different substrates. 0.7 gm of copper was used in each case. (I-L) The grain size distribution of copper coating on the above different substrates is fitted to appropriate distribution function. The polydispersity, $\delta$, and skewness, $S$. (M-P) The plots represent the distribution of aspect ratio of grains on above different substrates. The asphericity distribution factor $A = \sum l_i \Delta w_i$ is calculated by estimating the area under the curve for $0.60 < l_i < 0.75$. (Q-T) AFM scans of the above substrates at 500 nm x 500 nm scale. (U-X) AFM images of the substrates at 5 $\mu$m x 5 $\mu$m scale.
grains were examined to obtain the distribution in size and asphericity. The 2D packing efficiency was obtained by analysing the SEM images (Figure S2(g-l)) from which the fractional area covered by grains or the packing efficiency $\varphi_e$ was estimated by using MATLAB. The grayscale values for SEM images (Figure S2(g-l)) varied from one location to the other. Therefore, in order to obtain the representative data, 4–5 portions or islands were selected randomly from the SEM images (figure S8) which were then subjected to image analysis. For Trace paper, Printing paper, Drawing sheet, Sparkly paper, Circular patterned paper and Silicon wafer, the packing efficiency $\varphi_e$ were estimated as $0.96 \pm 0.01$, $0.91 \pm 0.01$, $0.88 \pm 0.01$, $0.83 \pm 0.05$, $0.86 \pm 0.01$ and $0.95 \pm 0.01$ respectively. The distribution of size and aspect ratio of grains for coatings on few different substrates are plotted in Figure 2I-P. The grain size distribution was fitted using Origin 2019. These figures suggest that for printing and trace papers, the grain size follows lognormal distribution with positive skewness, whereas for drawing paper, patterned paper and silicon wafer, the grain size follows Gaussian distribution with a high fraction of small size grains ($< 50$ nm) (Figure S4). In these plots, we have also presented the polydispersity, $\delta$ and skewness, $S$ as extracted from these fits. $\delta$ and $S$ could be calculated using two different methods: (a) by calculating mean $\mu$, and standard deviation $\sigma$, from the grain size data extracted by the above method and (b) by fitting the grain size data to known distribution curves to obtain $x_c$ (mean distribution size) and $w$ (distribution width parameter). The results presented in Table 2, S2, and S3 show that the calculated values for both these methods were comparable. The SEM images were analyzed in small islands and the size data were extracted by considering 40–50 randomly selected grains in each of these islands. Therefore, in order to interpet systematically the size data, the exact nature of the distribution that the grain sizes followed was required to be examined. Consequently, the $\delta$ and $S$ values derived from the resultant fits were used for subsequent results.

### Table 2

| Paper Number | 1 Trace Paper | 2 Printing Paper | 3 Drawing Paper | 4 Sparkle Paper | 5 Patterned Paper | 6 Silicon Wafer |
|--------------|---------------|------------------|-----------------|-----------------|-------------------|----------------|
| (a) Values calculated from distribution | | | | | | |
| Distribution | Lognormal | Gaussian | Lognormal | Gaussian | Lognormal | Gaussian |
| Equation | $y = \frac{B}{w\sqrt{\pi}} e^{-\frac{m^2}{2w^2}}$ | $y = \frac{B}{w\sqrt{\pi}} e^{-\frac{m^2}{2w^2}}$ | $y = \frac{B}{w\sqrt{\pi}} e^{-\frac{m^2}{2w^2}}$ | $y = \frac{B}{w\sqrt{\pi}} e^{-\frac{m^2}{2w^2}}$ | $y = \frac{B}{w\sqrt{\pi}} e^{-\frac{m^2}{2w^2}}$ | $y = \frac{B}{w\sqrt{\pi}} e^{-\frac{m^2}{2w^2}}$ |
| Adjusted R-Square | 1.00 | 0.97 | 1.00 | 0.97 | 1.00 | 0.98 |
| $x_c$ | $46.5 \pm 0.2$ | $68.8 \pm 1.8$ | $36.0 \pm 0.1$ | $40.5 \pm 0.5$ | $27.8 \pm 0.04$ | $32.0 \pm 0.6$ |
| $w$ | $0.2 \pm 0.0$ | $0.2 \pm 0.03$ | $16.0 \pm 0.2$ | $16.1 \pm 1.2$ | $12.9 \pm 0.1$ | $17.7 \pm 1.3$ |
| $B$ | $10.1 \pm 0.2$ | $10.5 \pm 1.1$ | $10.1 \pm 0.2$ | $9.8 \pm 0.7$ | $9.9 \pm 0.1$ | $9.7 \pm 0.7$ |
| PDI $\delta$ (from fitting) | 0.22 | 0.23 | 0.22 | 0.20 | 0.23 | 0.27 |
| Skewness $S$ (from fitting) | 0.68 | 0.69 | 0.00 | 0.00 | 0.00 | 0.00 |
| Asphericity $\gamma$ factor | 0.60 | 0.50 | 0.57 | 0.30 | 0.43 | 0.39 |
| (b) Values calculated directly from data of grain size | | | | | | |
| Mean $\mu$ (from Data) | 47.7 | 36.7 | 68.4 | 42.1 | 28.0 | 34.1 |
| Standard dev $\sigma$ (from Data) | 10.8 | 8.3 | 14.0 | 18.4 | 6.6 | 9.6 |
| PDI $\delta$ (from Data) | 0.22 | 0.23 | 0.20 | 0.20 | 0.23 | 0.28 |
| Skewness $S$ (from Data) | 0.67 | 0.68 | 0.02 | 0.02 | 0.05 | 0.09 |

### 3.3 Effect of quantity of copper used for coating on the resistance of the coated paper

To examine the effect of the quantity of copper used on the resistance of the copper coating, the Trace paper was used as the substrate while different quantity of copper $m_{Cu} = 0.05–0.8$ g was placed inside the heating coil. For estimating the thickness of the Cu coating thus formed, an indirect method had to be adopted, as the roughness of the substrate did not allow its accurate measurement. A small piece of the silicon wafer was attached to the substrate at the vicinity of its center using an adhesive, and the thickness of copper deposited on it was measured by AFM scanning (Figure S5). Variation of $t$ on trace paper was considered to be similar to that on the silicon wafer. The RPL for different coating decreased with increase in $t$ as presented in Figure 3A. Figure (3B-E, S5) shows the SEM images of copper-coated trace paper with increasing $m_{Cu} = 0.3$ to 0.8 g. The images in Figure 3B-E show that...
copper grains continued to be ellipsoidal, but the average grain size decreased with increase in $m_{Cu}$. In addition to surface heterogeneity, the grain shape and sizes are expected to be dependent on the energy of interaction of copper with the substrate. Copper-copper interaction is expected to be stronger (with zero interfacial energy) than the copper-paper interaction (finite value of interfacial energy). As a result, for the copper grains depositing on bare paper, interaction energy around it expected to be more heterogeneous spatially than that deposited on a layer of copper. Such heterogeneity can affect the crystal growth in different other systems.[36] As a result, the grains grow preferentially in one direction thereby assuming aspherical shape. The surface heterogeneity decreases with increase in $m_{Cu}$, leading to formation of more homogenized grains.[33,34] The plots in Figure 3F,G show the size (Figure 3F, S6) and asphericity distribution (Figure 3G, S7) of these grains, which were analyzed to obtain $\delta$ and $S$. In Figure 3H, the conductance of these different coatings, estimated as $\sigma = (RPL)^{-1}$ is plotted against $\varphi_e|_{exp}$. A quantitative relation was established between $\sigma$ and characteristics of the packing, importantly between $\varphi_e, \delta$ and $S$. For both Gaussian and Log-Normal distributions, the packing density $\varphi_e$ is known to increase with $\delta$ and $S$ of the distribution.[37–39] For spherical grains, this dependence can be expressed as\[^{[40]}\]

$$\varphi_e = \varphi_{RCP} + f(\delta, S) = \varphi_{RCP} + C_1\delta + C_2S\delta^2$$

(1)

in which $\varphi_{RCP}$ is the packing fraction of spherical grains with random close packing without any $S$ and $\delta$. In contrast to spherical grains, for ellipsoidal grains $\varphi_e$ is expected to depend also on asphericity, $l$ of grains. For a given substrate, the asphericity of grains varies according to the distribution as presented in figure (2(m-p), 3(g)). For mono-disperse ($r = \sqrt{ab} = \text{const.}$) ellipsoidal grains packing efficiency varies with asphericity ($l = b/a$ varying) as a bell curve\[^{[41,42]}\] However, for polydisperse grains the asphericity dependence on packing efficiency is not available in literature. The dependence of asphericity on packing efficiency can be extrapolated from mono-dispersed grains dependency as a weighted function. Therefore, the dependence on asphericity can be taken, $\varphi(l) = c_0 \sum_{i=0}^{1} l_i \Delta w_i + c_1 \sum_{i=0}^{1} l_i^2 \Delta w_i$, which $\Delta w_i$ correspond to the probability of finding grains of asphericity $l_i$. Since, by definition of asphericity $l_i < 1$, the effect of higher-order terms can be neglected. Considering all the above points, equation one can be simplified as, $\varphi_e = \varphi_{RCP} + f(\delta, S) \times \varphi(l) + \varphi_{RCP} \times \varphi(l)$. It has been shown earlier\[^{[41,42]}\] that randomly distributed ellipsoidal grains

---

**FIGURE 3** (A) Quantity of copper, $m_{Cu}$ used for coating a typical Trace paper was varied. The plot represents resistance per unit length (RPL) of coating and its estimated thickness $t$ as a function of $m_{Cu}$. (B-E) SEM images represent coatings of thickness 60, 97, 120 and 620 nm, respectively. The scale bar represents 200 nm. (F-G) The plots show the distribution of grain size and aspect ratio for the coating of different thickness. The curves 1–6 represent $m_{Cu} = 0.3, 0.4, 0.5, 0.6, 0.7$, and 0.8 gm, respectively. The curves in figure (F) are all fitted to Lognormal distribution. (H) The plot represents conductance of different coatings as a function of $\varphi_e|_{exp}$. The dashed line is a guide to the eye. The error bars represent the standard deviation of data from five sets of experiments.
FIGURE 4  (A) The plot shows that conductance $\sigma = (RPL)^{-1}$ of coating in various substrates scales linearly with packing fraction $\varphi_{eq1}$ calculated using equation 1 (represented by symbol ○). We have plotted here also the data $\sigma = (RPL)^{-1}$ vs $\varphi_{eq\exp}$ (represented by symbol □) as obtained from experiments. (B) The plot shows that data of conductance $\sigma$ and the packing efficiency $\varphi_{eq1}$ obtained for different substrates vary linearly with substrate roughness $\Delta_{5\mu m}$. The error bars represent the standard deviation of data from three sets of experiments.

pack more densely with a mixture of both spherical and aspherical grains.\[37\] For monodisperse ellipsoidal grains, maximum packing efficiency, $\varphi_{max}$ occurs at the aspect ratio of grains, $l_i \sim 0.66$, whereas for oblate and prolate spheroids, $\varphi_{max}$ occurs at $l_i = 0.6$ and 1.8, respectively.\[42\] For polydisperse ellipsoidal grains, $\varphi_{max}$ is achieved when a large fraction of grains are of $l_i = 0.66$.\[37\] It is then logical to consider that the fraction of grains, with asphericity varying from 0.60 to 0.75, is expected to contribute to the packing efficiency most significantly. Therefore, $A = \varphi(l) = c_0 \sum_{i=0.60}^{0.75} l_i \Delta w_i$ was considered to be proportional to the fractions of grains with asphericity from 0.60 to 0.75. Noting that the conductance of the coating varies linearly with the packing efficiency of the grains, as shown in Figure 3H, the data of conductance $\sigma$ from all different experiments were fitted to packing efficiency, calculated using,

$$\varphi_{eq1} = \varphi_{RCP} + (C_1 \delta + C_2 S) \sum_{i=0.60}^{0.75} l_i \Delta w_i \quad + (C_0 \varphi_{RCP}) \sum_{i=0.60}^{0.75} l_i \Delta w_i \quad$$

$$\varphi_{eq1} = \varphi_{RCP} + (C_1 \delta + C_2 S) A + (C_0 \varphi_{RCP}) A \quad$$

with $C_0, C_1$ and $C_2$ as the fitting parameters which account for the relative contribution of asphericity, $\delta$ and $S$ to the packing efficiency.

Figure 4A shows that this plot yields the fitting parameters, $C_1 = 0.4$, $C_2 = 0.25$ and $C_0 = 0.05$ with x-intercept as 0.82, which matches closely with the packing efficiency of random-close packing of spheres, that is, 0.8. In this figure, we also presented the data of $\sigma$ as a function of packing efficiency obtained from experiments, $\varphi_{eq\exp}$ (symbol □).

Finally, we have presented in figure 4B, the conductance $\sigma$ of different coatings and the packing efficiency, $\varphi_{eq1}$ against the roughness, $\Delta_{5\mu m}$ of the substrates. Since both $\sigma$ and $\varphi_{eq1}$ increase nearly linearly with $\Delta_{5\mu m}$, this data signifies that roughness of the substrate increases the packing efficiency of the grains, which results in increased conductance of the coating.

3.4 | Effect of layered or multiple coating on the resistance of the coated paper

SEM images presented in Figure 3 show that the change in $m_{Cu}$ effects the shape and size of copper grains. The RPL of the copper-coated trace paper was found to increase with decrease in the weight of copper in the coil. While the results presented in Figure 3 correspond to a single batch or layer of coating, the effect of number of layers on shape and size of the grains and consequently on the RPL was investigated. To explore this aspect, trace paper substrates were coated with copper inside vacuum coating unit (as described in Figure 1A), was cooled for 30 minutes and was then coated again with another layer of copper. The process was repeated over several cycles while keeping the total weight of copper loaded in the coil constant, $m_{Cu} = 0.8$gm. The samples 1–8 were coated as described in table S5. The bar chart in Figure 5A shows the variation of RPL for trace paper coated 1–4 times.

SEM images of these samples were analyzed to extract the grain sizes ($S_{10}$). Figure 5C and 5C show the grain size distribution and asphericity distribution for samples (1-8) obtained by analyzing SEM images. The mean grain size and the size of the distribution was found to increase with increase in number of coating, except in case of four layers.
The parameters $\delta$, $S$ and $A$ were calculated from the fits (figure S11, S12). The obtained parameters were used to calculate the effective packing efficiency using Equation 2. The conductance of trace paper electrode was found to increase linearly with the calculated packing efficiency $\varphi_{eq}$ (Figure 5D). The plot yields the fitting parameters, $C_1 = 0.4$, $C_2 = 0.25$ and $C_0 = 0.05$ with x-intercept as 0.83, which was similar to x intercept observed in Figure 4A. The RPL of the coated paper decreased with the amount of copper loaded in the coil for the initial coating process (Figure 5A (2-7)). Both double (Figure 5A (2-4)) and triple layered (Figure 5A (5-7)) coated papers show a similar trend. Similar to the $\varphi_{eq}$, RPL of the papers too was dominated by the $m_{Cu}$ of the initial layers. For example, RPL of the double-layered coated papers, was dominated by $m_{Cu}$ of the first layer; similarly, for three-layered coating, it was dominated by $m_{Cu}$ of the first two layers. It is possible that copper layers, deposited initially present a less heterogeneous substrate for the subsequent layers, thereby limiting both the asphericity and the size of the copper grains of these layers. A grain in free space can have growth in any direction and the introduction of other grains in the same space restrict the growth, directionality and orientation of the second grain. Similarly, for the coating of first few layers, limitations in orientation or condensation of grain may be smaller than for coating of subsequent layers. Hence the RPL of the coated paper is dominated by the initial coating process and the subsequent layering of the paper might not result in decrease of the RPL.

### 3.5 Effect of bending and creasing on the resistance of coated paper

We also examined the effect of cyclic bending (“U” shape) and creasing (“V” shape) of the copper-coated trace paper...
on the surface resistance. Figure 6A and 6B depict the images of the experiment. The coated paper was clipped between crocodile clippers of multimeter, and the resistance of coated paper was measured in response to variation of radius of curvature, $r_k$ (Figure 6A). The change in resistance of the paper was negligible compared to the change in $r_k$ (Figure 6C, Video VI), for example, resistance varied by 1.02 time for change in $r_k$ by an order of magnitude (Figure 5F). The change in resistance of coated paper was observed only when the paper was creased to $r_k < 20\text{mm}$. In a cyclic experiment, the coated trace paper was creased to a “V-shape” bent and was then increased (Figure 6B), repeatedly. The resistance of the uncreased trace paper was measured after every cycle. Multiple creasing of the trace paper to $r_k \sim 0\text{mm}$ (e.g., in V-shaped crease) resulted in rapid increase of the resistance to the point of crack formation in the coated layer (Figure 6C). Bending of the coated paper results in a negligible change in resistance ($r_k > 20\text{mm}$), but when the paper was creased to a “V-shape” ($r_k \sim 0\text{mm}$) bent over multiple times, for example, $N > 35$ cycles, crack appeared in the coating, with the resistance reaching infinity.

**4 | CONCLUSION**

The study presented here is different from that discussed earlier on the packing efficiency of isotropic cylindrical particles.[46] Whereas in the previous study authors compared packing of hard spheres with that of cylindrical rods that did not involve any directionality (aspect ratio increasing only in single direction) or even the cylindrical rods with aspect ratio less than 1, over here, we have compared the packing of ellipsoidal grains both prolate and oblate. In the previous study the packing of isotropic thin cylindrical rods was discussed, whereas we have discussed the packing efficiency of aspherical, polydisperse grains as a function of weighted summation of various aspect ratios. Furthermore, in contrast to several other studies on paper electrodes, that primarily focused on roughness in macro-scale,[20] we have for the first time, analyzed grain structure of vapor deposited copper coatings to show that micro-scale roughness of a substrate, for example, that of Trace paper and Printing paper leads to poly-dispersed ellipsoidal grains. Surface roughness at both scales affects the conductance of the coated layer. As the roughness at micro-scale increases, the grain becomes more aspherical and the packing efficiency. Such coating with large packing efficiency of grains yields large electrical conductance. In the other limit of substrates with large macro-scale roughness, for example, ones consisting of sharp corners, increase in surface roughness at macro-scale influences the integrity of the packing with the presence of micro-cracks at sharp edges, that decreases the conductance. For surfaces having intermediate roughness, the model presented here, relating the packing efficiency of grains to the polydispersity and skewness of size and asphericity distribution is expected to be useful also for determining the conductance of different other metal coatings on similar substrates. The conductivity of coated surfaces varied linearly with calculated packing efficiency $\varphi_c |_{\text{eq1}}$. In the case of multiple coating on the substrate, the grain
shape and size are controlled by the amount of copper used in the coil for the first layer of coating. The resistance of coated paper, in experiment with cyclic bending and relaxing, changes insignificantly for bending radius of curvature larger than 1 cm and changes drastically for smaller radii of curvature. These copper coated trace papers is expected to be useful for various applications, e.g. as functional electrodes in designing flexible capacitive pressure sensor.

5 | EXPERIMENTAL SECTION

5.1 | Coating of material

A high vacuum coating unit (Hind High vacuum Co. (P) Ltd., Model: 12A4D) was used thermal evaporation and deposition of copper on the substrate. A flat sheet of paper was placed above a tungsten coil inside the closed chamber of a vacuum coating unit. The desired quantity of copper (Cu) placed inside a tungsten coil was heated inside the chamber maintained at $10^{-5}$ bar pressure. The exposure time and current were maintained at 30 second and 60 amp, respectively. Cu evaporates inside the coil, diffuses out of it and then condenses on a substrate positioned vertically above the coil.

5.2 | Measurement of electrical resistance

The electrical resistance of the copper layer on different substrates was measured via two different methods: by using a multimeter (Figure S1(b)) and Electrochemical Impedance (Autolab PGSTAT302N) (Figure S1(c)). The DC resistance of the coated paper was measured as a function of length using a digital multimeter. The impedance of coated paper was measured by applying a potential of 5mv with a frequency range of 1 mHz to 10,000 Hz using two electrode system Electrochemical Impedance Spectroscopy (EIS).

5.3 | Surface topography

The topography of the substrates before and after coating with copper was examined by carrying out Scanning Electron Microscopy (SEM) (SUPRA 40 VP and CARL ZEISS EVO 50) of the surfaces (Figure S2(a-r)). Surface topography of the sample was also assessed using AFM. The sample surface was scanned using Peak force scanning mode of Bruker Multimode 8 AFM (Scan Assyst Air Tip) (Figure S2(I-VI)).

5.4 | Measurement of thickness of copper coating

The thickness of the copper layer was measured using an Atomic Force Microscope (Bruker Multimode 8). Tapping mode of AFM was used to image the copper surface (figure S3(a, b)) (TAP 150 silicon-nitride tip). The radial thickness change in the coating for trace paper was measured by Contact Mode Profilometry (figure S3(c, d)) (Bruker Dektak XTL).

5.5 | Analysis

5.5.1 | Image processing and grain size measurement

Grain size measurements of copper grains from SEM images was done using Microsoft PowerPoint. Random grains were enclosed with ellipses, and both major and minor axis diameters were extracted (figure S2(g), S5(a-f)). The size of the grains was estimated as $\sqrt{ab}$, where $a$ and $b$ are the lengths of the major and minor axis, respectively. The asphericity of the grains was measured as $b/a$ (less than or equal to 1). The fractional area coverage or the 2D packing efficiency was estimated using MATLAB (figure S8(a,b)). The Grain size distribution was fitted using Origin2019 (figure S4, S6).

5.5.2 | Surface roughness

Surface roughness of the substrates was measured using AFM (Bruker Multimode 8). The samples were scanned using Peak force mode (Scan Assyt tip, Silicon nitride tip $k = 0.4N/m$) (figure S9). Surface roughness at scales 500 nm, 5 $\mu m$ & 10 $\mu m$ were obtained from AFM scans (figure S9(g)). Dektak contact mode profilometer was used to measure the surface roughness at 200 $\mu m$ and 500 $\mu m$ scale (figure S9(h-j)).

5.5.3 | Surface energy

The static contact angle of DI(De-Ionised) water and Pentadecane was measured on the substrates. The surface energy of the paper was then calculated by applying the Owens and Wendt model (figure S13).

5.5.4 | Interfacial adhesion

Scotch tape test was performed to test the bonding of the copper with the substrate. The tape was first brought in
contact with the copper coating and then peeled off. As shown in figure S16 even after repeated peeling of the Scotch tape there was no visible amount of copper that came off the substrate.

ACKNOWLEDGMENT
A.G. acknowledges financial assistance Department of Science and Technology as grant no. SB/S3/CE/036/2013 for this work.

DATA AVAILABILITY STATEMENT
Research data are not shared.

ORCID
Gaurav Rawal https://orcid.org/0000-0001-6108-930X
Animangsu Ghatak https://orcid.org/0000-0002-1527-3824

REFERENCES
1. C. Pang, G.-Y.Y. Lee, T. Il.Kim, S.M. Kim, H.N. Kim, S.-H.H. Ahn, K.-Y.Y. Suh, Nat. Mater. 2012, 11, 795.
2. H. Kang, S. Jung, S. Jeong, G. Kim, K. Lee, Nat. Commun. 2015, 6, 1.
3. S.C.B.B. Mannsfeld, B.C.-K. Tee, R.M. Stoltenberg, C.V.H.H.-H. Chen, S. Barman, B.V.O.O. Muir, A.N. Sokolov, C. Reese, Z. Bao, Nat. Mater. 2010, 9, 895.
4. L. Nyholm, G. Nyström, A. Mihranyan, M. Strømme, Adv. Mater. 2011, 23, 3751.
5. L. Hu, J.W. Choi, Y. Yang, S. Jeong, F. La Mantia, L.F.-L. F. Cui, Y. Cui, Proc. Natl. Acad. Sci. 2009, 106, 21490.
6. Y. Lin, D. Gritsenko, Q. Liu, X. Lu, J. Xu, ACS Appl. Mater. Interfaces. 2016, 8, 20501.
7. H. Gullapalli, V.S.M. Vemuru, A. Kumar, A. Botello-Mendez, R. Vajtai, M. Terrones, S. Nagarajah, P.M. Ajayan, Small 2010, 6, 1641.
8. A. Manekkathodi, M.-Y.Y. Lu, C.W. Wang, L.-J.J. Chen, Adv. Mater. 2010, 22, 4059.
9. A. Araújo, A. Pimentel, M.J. Oliveira, M.J. Mendes, R. Franco, E. Fortunato, H. Águas, R. Martins, Flex. Print. Electron. 2017, 2, 1.
10. V. Kumar, S. Forsberg, A.-C. Engström, M. Nurmii, B. Andres, C. Dahlström, M. Toivakka, Flex. Print. Electron. 2017, 2, 035002.
11. H.M. Lee, S.Y. Choi, A. Jung, S.H. Ko, Angew. Chemie - Int. Ed. 2013, 52, 7718.
12. L. Hu, Y. Cui, Energy Environ. Sci. 2012, 5, 6423.
13. L.-Q. Tao, K.-N. Zhang, H. Tian, Y. Liu, D.-Y. Wang, Y.-Q. Chen, Y. Yang, T.-L. Ren, ACS Nano 2017, 11, acs.nano.7b02826.
14. S. Yin, W. Zhu, Y. Deng, Y. Peng, S. Shen, Y. Tu, Mater. Des. 2017, 116, 524.
15. D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G.Q. Lu, H.-M. Cheng, ACS Nano 2009, 3, 1745.
16. C. Preston, Z. Fang, J. Murray, H. Zhu, J. Dai, J.N. Munday, L. Hu, J. Mater. Chem. C. 2014, 2, 1248.
17. D. Tobjörk, R. Österbacka, Adv. Mater. 2011, 23, 1935.
18. P. Italainen, A. Määttänen, J. Järnström, D. Tobjörk, R. Österbacka, J. Peltonen, Ind. Eng. Chem. Res. 2012, 51, 6025.
19. A. Russo, B.Y. Ahn, J.J. Adams, E.B. Duoss, J.T. Bernhard, J.A. Lewis, Adv. Mater. 2011, 23, 3426.
20. A.C. Siegel, S.T. Phillips, M.D. Dickey, N. Lu, Z. Suo, G.M. Whitesides, Adv. Funct. Mater. 2010, 20, 28.
21. S. Yeniyol, N. Bölükbaşi, A. Bilir, A.F. Çakır, M. Yeniöyl, T. Ozdemir, ISRN Biomater. 2013, 2013, 1.
22. M.R. Amirzada, A. Tatzel, V. Vierreck, H. Hillmer, Appl. Nanosci. 2016, 6, 215.
23. D.J. Cohen, D. Mitra, K. Peterson, M.M. Maharbiz, Nano Lett. 2012, 12, 1821.
24. Y. Zheng, Z. He, Y. Gao, J. Liu, Sci. Rep. 2013, 3, 1.
25. J.H. Johnston, J. Moraes, T. Borrmann, in Synth. Met., Elsevier 2005, 65.
26. H.M. Kim, K. Kim, C.Y. Lee, J. Joo, S.J. Cho, H.S. Yoon, D.A. Pejaković, J.W. Yoo, A.J. Epstein, Appl. Phys. Lett. 2004, 84, 589.
27. S. Ahmed, M.N. Bui, A. Abbas, 2016, 77, 249.
28. J.C. Cunningham, P.R. DeGregory, R.M. Crooks, Annu. Rev. Anal. Chem. 2016, 9, 183.
29. A.P.M. Tavares, N.S. Ferreira, L.A.A.N.A. Truta, M.G.F. Sales, Sci. Rep. 2016, 6, 26132.
30. A. Rudawska, E. Jacniacka, Int. J. Adhes. Adhes. 2009, 29, 451.
31. R.J. Good, L.A. Girifalco, J. Phys. Chem. 1960, 64, 561.
32. P.A. Gabrys, S.E. Seo, M.X. Wang, E. Oh, R.J. Macfarlane, C.A. Mirkin, Nano Lett. 2018, 18, 579.
33. P.P. Nampi, S. Kume, Y. Hotta, K. Watari, Bull. Mater. Sci. 2011, 34, 799.
34. C.V Thompson, Annu. Rev. Mater. Sci. 1990, 20, 245.
35. C.A. Handwerker, P.A. Morris, R.L. Coble, J. Am. Ceram. Soc. 1989, 72, 130.
36. M. Muthukumar, J. Chem. Phys. 2009, 130, 161101.
37. A. V. Krylyuk, A.P. Philipse, Phys. Status Solidi. 2011, 208, 2299.
38. D.-H.H. Nguyen, E. Azéma, F. Radjai, P. Sornay, Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys. 2014, 90, 012202.
39. X. Garcia, L.T. Akanji, M.J. Blunt, S.K. Matthai, J.P. Latham, Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys. 2009, 80, 1.
40. K.W. Desmond, E.R. Weeks, Phys. Rev. E 2014, 90, 022204.
41. Y. Stoyan, A. Pankratov, T. Romanova, A. Pankratov, T. Romanova, J. Glob. Optim. 2016, 65, 283.
42. Z.Y. Zhou, R.P. Zou, D. Pinson, A.B. Yu, Ind. Eng. Chem. Res. 2011, 50, 9787.
43. C.W. Lan, W.C. Lan, T.F. Lee, A. Yu, Y.M. Yang, W.C. Hsu, B. Hsu, A. Yang, in J. Cryst. Growth, North-Holland 2012, 68.
44. S. Gokhale, K.H. Nagamanasa, V. Santhosh, A.K. Sood, R. Ganapathy, Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 20314.
45. N. D’Souza, M.G. Ardakani, A. Wagner, B.A. Shollock, M. McLean, J. Mater. Sci. 2002, 37, 481.
46. A.P. Philipse, Langmuir 1996, 12, 1127.

SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: G. Rawal, A. Ghatak. Effect of roughness on the conductivity of vacuum coated flexible paper electrodes. Nano Select 2021, 1-12. https://doi.org/10.1002/nano.202100034