Oxidation kinetics of nanoscale copper films studied by terahertz transmission spectroscopy

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Terahertz (THz) transmission spectroscopy is used to measure the oxidation kinetics of copper thin films evaporated on silicon substrates. The transmission of broadband THz pulses from 1 to 7 THz through the copper film is measured while it gets oxidized at an elevated temperature in ambient air. The change in the transmitted THz electric field is correlated with the growth of the cuprous oxide layer and the decrease in thickness of the copper layer. Oxidation curves were obtained for heating temperatures of 120–150 °C and were found to follow a parabolic rate law. Using the Arrhenius equation, we calculate an activation energy for diffusion of 0.55 eV. By measuring the THz transmission through unoxidized copper layers of several thicknesses, we also measured the optical properties of thin copper films around the percolation threshold thickness of 7 nm. Around the percolation transition, the optical properties of freshly deposited copper thin films are very different from that of copper layers of the same thickness remaining after partial oxidation of thick copper films. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4729808]

I. INTRODUCTION

Copper and copper-based alloys are very popular for use in the electronics and optoelectronics industry because of their low cost, high thermal and electrical conductivity, and ease of fabrication. For example, copper is preferred over aluminium in ultra large scale integration devices for use as an interconnect material because of its low electrical resistivity.[1,2] Copper foils are also used as the conductive element in flexible circuits. However, the surface of copper easily oxidizes and the oxide layer formed does not provide enough protection to prevent further oxidation.[3] Oxidation is an important factor, which degrades the performance of copper based electronic devices.[4]

Copper is also an important material for terahertz (THz) applications. Due to the high conductivity, copper can be used for metal wire and parallel plate THz waveguides[5–7] and for the production of sharp tips in aperture-less near field scanning optical microscopy.[8] The presence of even a thin oxide layer on a metal surface can, in principle, distort the propagation of THz surface waves.[9] This occurs because the surface wave propagates along the wire and interacts with this thin layer over a long propagation distance of several cm or more. Hence, it is interesting to study the oxidation of copper and the effect it has on the THz optical properties of copper surfaces.

In the past, different techniques have been employed to measure the oxidation of copper and copper thin films.[10–13] Njeh *et al.*[10] discuss the oxidation of copper thin films in air using x-ray reflectometry and x-ray diffraction at temperatures below 250 °C. Ellipsometry, using 350 nm to 850 nm light, has also been employed successfully to characterize the oxidation kinetics by Iijima *et al.*[11] It was shown by Zhong *et al.*[12] that the measurement of the sheet resistance of copper layers during oxidation can also give information about the oxidation kinetics. In the latter technique, the change in sheet resistance was correlated with the thinning of the copper metal layer due to oxidation. Transmission electron microscopy has also been used to obtain insight into the initial stages of oxidation.[13] All these techniques, however, either provide little information on the optical properties of copper during the various stages of oxidation of a copper surface or require physical contact to be made with the copper, which may influence the measurement.

In this paper, the oxidation kinetics of Cu films at elevated temperatures in the range of 120 to 150 °C in air is studied by non-contact, *in situ* transmission measurements of broadband terahertz pulses. Copper being a good conductor, the THz transmission is initially very low. We find that, as the film is heated and the copper oxidizes, the transmission of THz light gradually increases. The THz electric field amplitude transmitted by a freshly deposited 21 nm thick copper film is about 5% of the field amplitude incident on the film. While heated at a temperature of 150 °C, this number increases to 100% in about 30 min. In contrast, when heated at a temperature of 130 °C for 3 h, the transmitted amplitude is only about 38% of the incident field amplitude. Using the measured THz conductivity of an un-oxidized copper film, we can determine the instantaneous thickness of the copper layer and the thickness of the cuprous oxide layer during oxidation from the instantaneous THz transmission. The oxidation rate determined in this way is found to follow a parabolic law for the oxide growth, with an activation energy of diffusion of 0.55 ± 0.06 eV.

II. EXPERIMENT

The copper thin films were fabricated using electron beam evaporation. The films were evaporated onto clean, high resistivity silicon substrates by an e-beam evaporator in
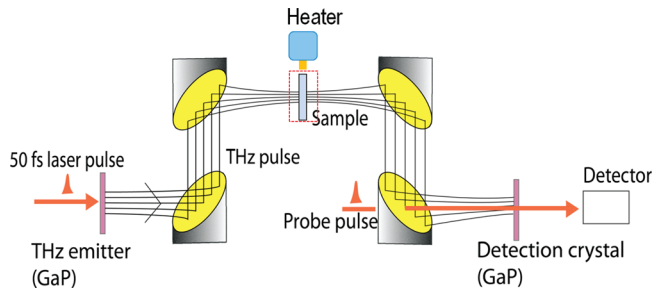
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FIG. 1. Broadband THz time domain spectroscopy set-up.

a vacuum of 1×10^{-4} Pa. The thickness of the evaporated thin film is measured using a quartz crystal resonator positioned inside the evaporation chamber. The evaporation rate used to prepare the samples was 1 Ås^{-1}. X-ray diffraction measurements of evaporated samples show that the evaporated Cu films are polycrystalline in nature. To heat the copper film, the sample was sandwiched between two copper plates, connected to a soldering iron. A thermal paste was used to ensure a good thermal contact between the mount and the sample. To measure the temperature of the sample, we also inserted a thermocouple in a small space between the two copper plates. Using this arrangement, we are able to heat the sample at a specified temperature up to 250 °C. For the THz transmission measurement, the heating mount with the sample is positioned at the focus of the THz beam. Holes of 3 mm diameter were drilled into the copper plates to allow transmission of the THz beam through the sample.

The experimental set-up used for our THz transmission measurements is schematically shown in Fig. 1. We use 50 fs laser pulses with a center wavelength of 800 nm from a Ti:sapphire oscillator (Scientific XL, Femtolasers, Vienna) with an average power of 2.5 W and a repetition rate of 5.2 MHz. The laser beam is split into a pump beam and a probe beam by a 90:10 beam splitter. The high power beam is used as the pump beam to generate single cycle THz pulses from a 300 μm thick (110) GaP crystal by optical rectification. Optical rectification can be interpreted as difference frequency mixing of the frequencies within the bandwidth of the femtosecond laser pulses giving rise to the creation of THz photons. The generated THz pulses are collected, collimated, and focussed onto the sample using two parabolic mirrors. Another two parabolic mirrors collect and focus the beam again onto another 300 μm GaP crystal, which acts as electro-optic detection crystal.[14,15] The probe beam is also focussed onto the electro-optic detection crystal

through a hole in the last parabolic mirror. In the electro-optic crystal, the instantaneous electric field of the THz pulse elliptically polarizes the probe beam. The ellipticity induced in the probe beam is measured using a system of a quarter wave plate, a Wollaston prism, and a differential detector and is proportional to the instantaneous THz electric field. Since the detection efficiency also depends on the azimuthal angle of the crystal, the crystal is rotated around the surface normal to maximize the signal. The strongest detected signals are obtained when the angle between the 800 nm probe polarization and the THz polarization is either 90° or 0°.[16] The pump pulses, and hence the THz pulses, are delayed using a retro-reflecting mirror arrangement mounted on a loudspeaker oscillating at 50 Hz. By varying the delay between the THz and probe pulses, we can measure the THz electric field in a stroboscopic manner. In this way, we get a 25 ps long THz electric field time trace, every 20 ms.[17]

III. RESULTS

Fig. 2(a) shows the temporal waveform of a typical THz pulse detected after passing through a 9 nm thick copper film on a thick silicon wafer. For reference, the THz pulse detected after passing through an uncoated silicon wafer is also shown. The detected THz electric field consists of almost a single cycle. The rapidly oscillating tail following the main pulse is due to the phase mismatch between the pump laser pulses and the THz pulses in the generation crystal.[14] By performing a fast Fourier transform of the temporal data, we obtain the amplitude spectra of the pulses as shown in Fig. 2(b). The ultrafast THz pulses are seen to contain usable spectral components in a wide bandwidth from 0.5 to 7 THz.

Fig. 3 shows the normalized peak-to-peak value of the electric field of the THz pulses transmitted through the copper films, as a function of time. The films were heated at temperatures of 120, 130, 140, and 150 °C. The initial thickness of the copper films used for the oxidation measurement is 21 nm. The THz transmission through a freshly deposited 21 nm thick copper film is very low. However, as the film is heated, the THz transmission increases with time. The rate of increase is much higher at a temperature of 150 °C than at 120 °C, even though the temperature difference is only 30 °C. For the three highest temperatures used, the transmission reached its highest, final value within 3 h, suggesting that the oxidation is complete. For the lowest temperature, the transmission continues to increase even after this time.
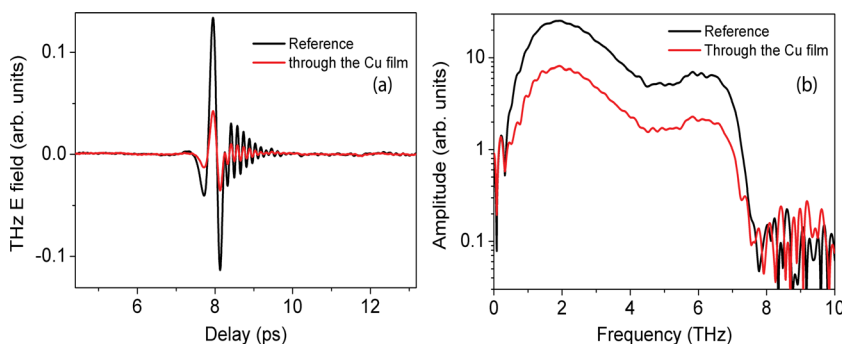

FIG. 2. (a) Electric field of the THz pulse transmitted through a silicon wafer with (red) and without (black) a thin copper film. The copper film thickness is 9 nm. (b) Amplitude spectra obtained after Fourier transforming the electric field of the THz pulses.
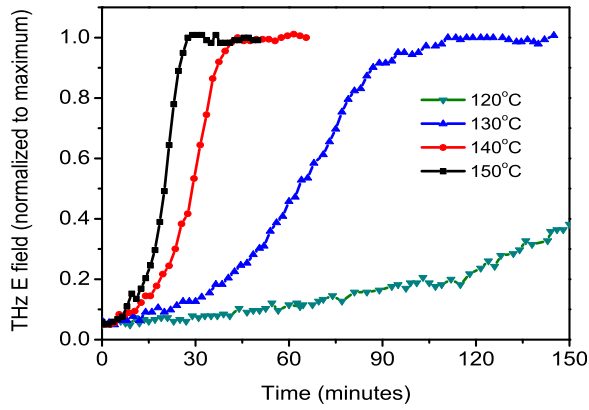
FIG. 3. The peak-to-peak value of THz pulses transmitted through oxidizing copper films at different temperatures, as a function of time.

$$\frac{\tilde{E}_{tx}}{\tilde{E}_{ref}} = \frac{1+n}{1+n+Z_0\tilde{\sigma}(\omega)d}, \tag{1}$$

where $\tilde{E}_{tx}$ is the amplitude of the THz electric field transmitted through the copper film, $\tilde{E}_{ref}$ is the transmitted electric field through the uncoated half of the silicon wafer, Z_0 is the impedance of free space (see also Fig. 4(a)), d is the thickness of the copper film, $n_3 = 3.418$ (Ref. 23) is the frequency-independent refractive index of silicon at THz frequencies, and $\tilde{\sigma}(\omega)$ is the complex conductivity of the film. If we know the conductivity of the thin film, we can calculate the THz transmission as a function of thickness from Eq. (1). For a thin film, the conductivity is expected to be lower than that of bulk metal, due to the large number of intrinsic defects created during physical vapor deposition.[24,25] The electron-beam evaporated films are polycrystalline, with distinct grain boundaries. Scattering from these grain boundaries considerably influences the properties of the film. This results in a lower conductivity of evaporated thin films compared to that of bulk metal. Hence, we adjusted the value of the conductivity of copper, so as to match the measured value of the THz transmission through a thick copper film of 37 nm. This gives a conductivity value of $\sigma = 1.8 \times 10^7$ Sm^{-1}. This should be compared to the dc bulk conductivity value of copper, $\sigma = 5.6 \times 10^7$ Sm^{-1}. The conductivity is assumed to be real and frequency independent for the low THz frequencies. Since the THz transmission seems to be frequency-independent, only a single frequency was used in the calculation. The calculated THz transmission for copper films of different thickness is shown in Fig. 4(b).

We also measured the THz transmission of un-oxidized copper films of various, known, thicknesses ranging from 3 to 37 nm. Only half of the wafer was covered with the copper film and the other half was masked during evaporation (Fig. 4(a)). The THz transmission through the copper film and through the uncovered half of the silicon wafer was measured for each of these samples. The transmission was measured on the same day as the films were deposited, so as to minimize errors due to oxidation at room temperature. The THz beam path in the set-up was flushed with dry nitrogen gas to reduce absorption of THz light by water vapor molecules in the ambient atmosphere. In Fig. 4(b), the measured THz intensity transmitted through the copper film with respect to the transmission through an uncoated silicon wafer

Apparently, at this temperature, the oxidation is incomplete even after 3 h.

Copper can oxidize to form two oxides, cuprous oxide (Cu_2O) or cupric oxide (CuO). However, for heating temperatures below 225 °C, it is known that the oxide formed is predominantly cuprous oxide.[18] Hence, at any particular instant of time during oxidation, the sample consists of the silicon substrate, a remaining copper layer, and a cuprous oxide layer formed due to heating. A thin layer of cuprous oxide fully transmits the THz pulses, as do most dielectric, nonabsorbing layers which are much thinner than the wavelength of the light used. In our case, the oxide film is a few nanometers thick, whereas the wavelength is around 300 μm. For the same reason, we can also neglect the reflection losses at the Cu_2O-air interface. Therefore, the transmission through the oxidizing sample depends only on the thickness of the copper film. If we know which thickness of the copper film corresponds to a particular value of the THz transmission, we can determine the instantaneous remaining copper film thickness during oxidation.

It is tempting to calibrate our measurement by performing the THz transmission experiments on un-oxidized copper films of varying thickness, and to correlate this with the instantaneous transmission of the originally 21 nm thick film during oxidation. However, as we will show now, this leads to erroneous results. First, we attempt to model the transmission of a copper thin film using the transmission equation:[19–22]
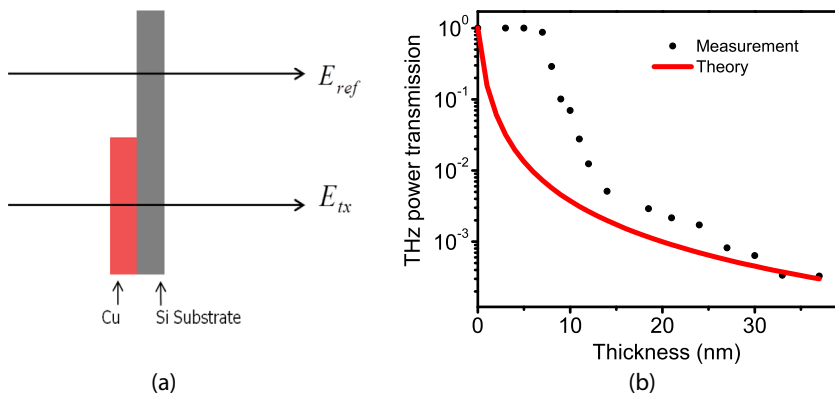

(a)

(b)

FIG. 4. (a) Schematic of thin film samples prepared for the measurement of THz transmission through copper thin films. (b) THz transmission through Cu films as a function of thickness: Circles indicate the experimental results and the solid line shows the theoretical transmission calculated according to Eq. (1) for a uniform copper film.
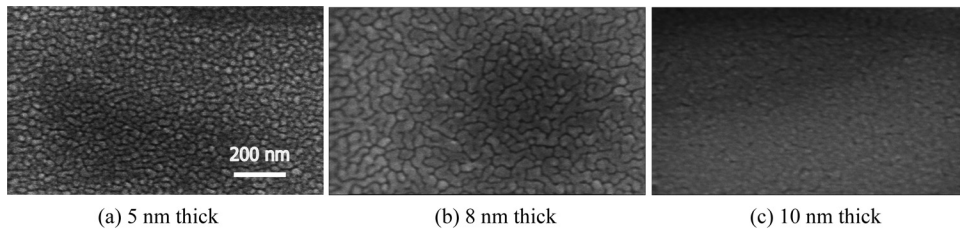
FIG. 5. Scanning electron micrographs of thin copper films on silicon substrates, with thickness around the percolation threshold.

(a) 5 nm thick   (b) 8 nm thick   (c) 10 nm thick

is also plotted. Starting from the thickest films, the transmission rapidly increases for decreasing film thickness, as expected. However, the transmission does not reach its maximum value when the film thickness reaches a value of 0 nm, but already at a thickness of about 7 nm. This contrasts with the transmitted THz power calculated using Eq. (1), which shows a transmission which gradually increases to 100% when the copper thickness becomes zero.

To understand why this is the case, we show in Fig. 5 the SEM images of the copper films for three different thicknesses: 5, 8, and 10 nm. The images show that these ultra thin films do not form a smooth uniform layer. The unexpected increase in the THz transmission for films of thickness <8 nm can be explained on the basis of this non-uniform film morphology.[24] Formation of thin films by physical vapor deposition is characterized by the formation of nuclei and their subsequent growth. As the deposition continues, the nucleated metal islands grow until they coalesce to form a continuous macroscopic network. The transition from isolated islands to a connected network occurs at the so-called percolation threshold thickness, which is the effective thickness at which the electrons can completely percolate through the random metal network. Below the percolation threshold, the electrons cannot move out of the metal islands and hence the film behaves more like an insulator. For films having an effective thickness above the percolation threshold, the conductivity is still reduced with respect to the bulk value because of carrier scattering by the film inhomogeneities. The SEM images indicate that the percolation threshold occurs somewhere between 5 and 8 nm. This agrees with the percolation threshold determined from the experimental THz transmission data shown in Fig. 4(b). Similar results were reported and extensively studied by Walther *et al.*, for thin gold films.[22]

We can now understand why we cannot calibrate our oxidation measurements using the measured transmission of unoxidized copper films of varying thickness. Percolation considerably influences the conductivity of the deposited films. An unoxidized Cu film of 6 nm thickness will not have the same optical properties as an oxidizing copper film of which 6 nm remains as copper. The former is made up of mostly disconnected copper islands whereas the latter largely retains the optical properties of the originally 21 nm thick copper layer.

A better way to calibrate our measurements is to measure the conductivity of the unoxidized 21 nm thick copper film, where we assume that as the film oxidizes, the conductivity of the remaining copper does not change. In that case, the changes in the THz transmission are caused by changes in the thickness of the remaining copper layer only. For a fully oxidized copper film, no significant differences in the THz transmission were observed for samples held at T = 150 °C, and samples cooled down to room temperature. This suggests that thermal changes in the conductivity, which could in principle affect the calibration procedure, were negligible.

The average conductivity of the 21 nm thick copper films used for oxidation measurement later was measured to be $(1.14 \pm 0.04) \times 10^7$ Sm^{-1}. Applying Eq. (1) to the THz transmission measurement of oxidizing copper films (Fig. 3), we back-calculated the instantaneous copper thickness during oxidation. This is shown in Fig. 6(a), where we plot this calculated copper thickness as a function of oxidation time. The maximum value of the THz transmission is reached when the oxidation is complete, and is used as E_{ref} in this case. The THz transmission through the thicker films is considerably lower, which gives a lower signal-to-noise ratio. This explains the larger scatter of the data points in the calculated instantaneous copper thickness in the early stages of the oxidation. Using a surface profilometer, we have measured the thickness of several copper films before and after complete oxidation. When completely oxidized, the thickness of the
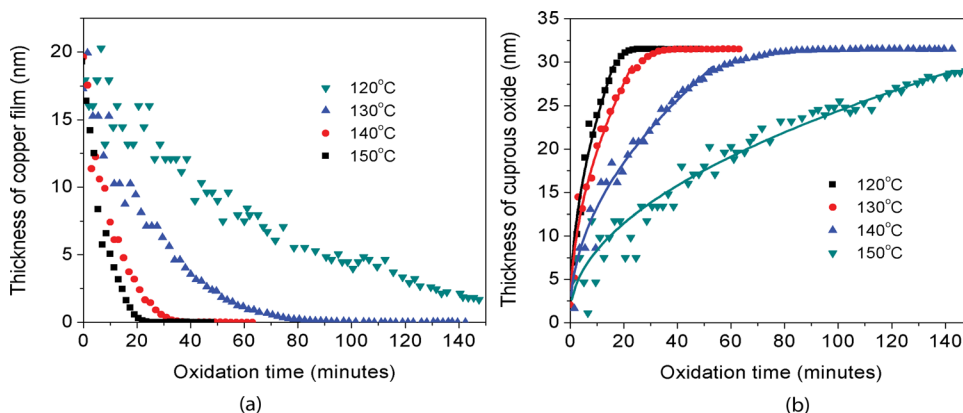

FIG. 6. (a) The instantaneous copper film thickness during oxidation as a function of time after calibration. (b) The instantaneous cuprous oxide thickness as a function of time. The used-up copper thickness is multiplied by a factor of 1.5 to obtain the final oxidation curve.

(a)

(b)

oxide layer is around 1.5 times that of the pure copper layer. To calculate the instantaneous cuprous oxide thickness during oxidation, we multiplied the used-up copper thickness by this experimentally determined factor 1.5, which gives us the instantaneous Cu_2O thickness. The growth of the cuprous oxide layer as a function of time is shown in Fig. 6(b). When the copper film is completely oxidized, the oxide layer does not grow further. This explains the saturation in the growth of the cuprous oxide thickness after a certain time.

IV. DISCUSSION

We can further analyze the temperature dependence of the oxidation rate. In the temperature range we used, the oxidation of copper is expected to follow a parabolic rate law:[12,26]

$$d_{oxide} = d_0 + k(T)t^{\frac{1}{2}}, \qquad (2)$$

where d_{oxide} is the thickness of the oxide layer at time t, $k(T)$ is the rate constant, and d_0 is the natural oxide layer on the copper film formed at room temperature before heating the sample. Equation (2) is fitted to the oxide growth curves shown in Fig. 6(b). A natural oxide layer of $d_0 = 1$ nm was assumed for all the films to obtain the best fit for the measurements. When oxidation is complete, the thickness of the cuprous oxide no longer increases. Hence, the part of the curve where the thickness remains constant is not used in the fitting procedure. Generally, a parabolic rate law for the oxidation of copper thin films implies a diffusion-dominated oxidation process.[27] The activation energy for diffusion can be obtained from the temperature dependence of the rate constant k, which follows the Arrhenius equation:[28]

$$k(T) = k_0 e^{\frac{-E_a}{R}\frac{1}{T}}. \qquad (3)$$

Here, k_0 is a constant, E_a is the activation energy for diffusion, $R = 8.314$ J mol^{-1} K^{-1} is the universal gas constant, and T is the heating temperature. If we plot $\ln(k)$ against $\frac{1}{T}$, the slope of the straight line thus obtained is $\frac{-E_a}{R}$. Hence, the value of the activation energy can be determined from the slope of the Arrhenius curve. The Arrhenius relation for rate constants obtained from fitting equation (2) to our oxidation data is plotted in Fig. 7. The activation energy for diffusion calculated from the slope of a straight line fit to these data is 0.55 ± 0.06 eV.
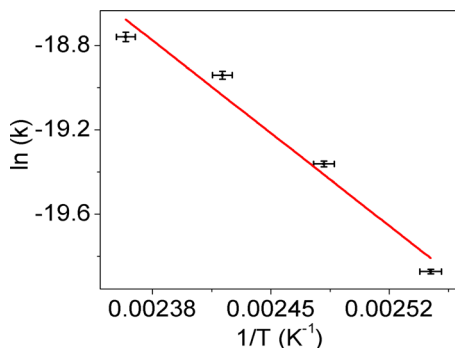

FIG. 7. Arrhenius plot of $\ln(k)$ versus $\frac{1}{T}$. The red line is a linear fit to the measurement.

When a copper film is exposed to air, a native layer of oxide quickly forms on the surface of the metal film. For further oxidation to be possible, Cu^+ ions have to be transported from the copper film to the interface between oxide and air by diffusion.[29] The activation energy for diffusion of Cu^+ ions through the motion of vacant Cu^+ sites in the opposite direction is at least the bond energy of copper, 2 eV.[12,30] However, the diffusion along a grain boundary can be much faster than the volume diffusion through defects in the material's crystal structure.[28] Since the activation energy calculated from our measurements is much lower than 2 eV, we assume that the diffusion mechanism is mostly grain boundary diffusion. The activation energy of 0.55 ± 0.06 eV that we obtain is somewhat higher than that reported by Gao et al.[31] for Cu thin films at heating temperatures of 175–400 °C (0.37 eV) and comparable to that reported by Zhong et al.[12] for Cu thin films at temperatures of 180–260 °C (0.57 eV).

V. CONCLUSIONS

The oxidation of copper thin films on silicon substrates was studied using THz time domain spectroscopy in the temperature range of 120–150 °C. We find that the oxidation kinetics could be obtained by measuring the THz transmission through the heated copper films as a function of time. By relating the instantaneous transmission of the oxidizing copper films with the calculated transmission based on the measured conductivity of the copper, we were able to obtain the instantaneous copper layer thickness and, thus, the cuprous oxide layer thickness during the oxidation. Calibrating the measured THz transmission during the oxidation by comparison with the measured THz transmission through unoxidized copper layers of several thicknesses is not possible. We show that this is explained by the percolation transition of copper that occurs for average copper layer thicknesses around 7 nm. Such a transition is absent in layers of the same thickness, which result from the oxidation of a layer with a much larger starting thickness. The oxidation follows a parabolic rate law from which the activation energy for diffusion is calculated to be 0.55 ± 0.06 eV. This value suggests a fast diffusion mechanism, such as diffusion of Cu atoms through the grain boundaries as the dominant diffusion mechanism.

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