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Mariampillai et al.

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[redacted]

N-HETEROCYCLIC CARBENES

C23F 1/10 (2006.01)
(52) **U.S. Cl.**

(71) [redacted] QUEEN'S UNIVERSITY AT

[redacted]

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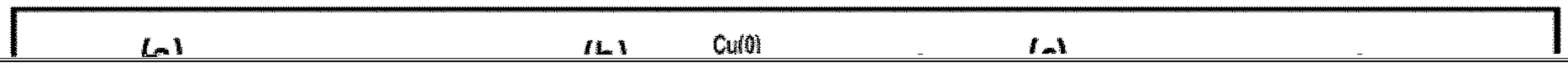
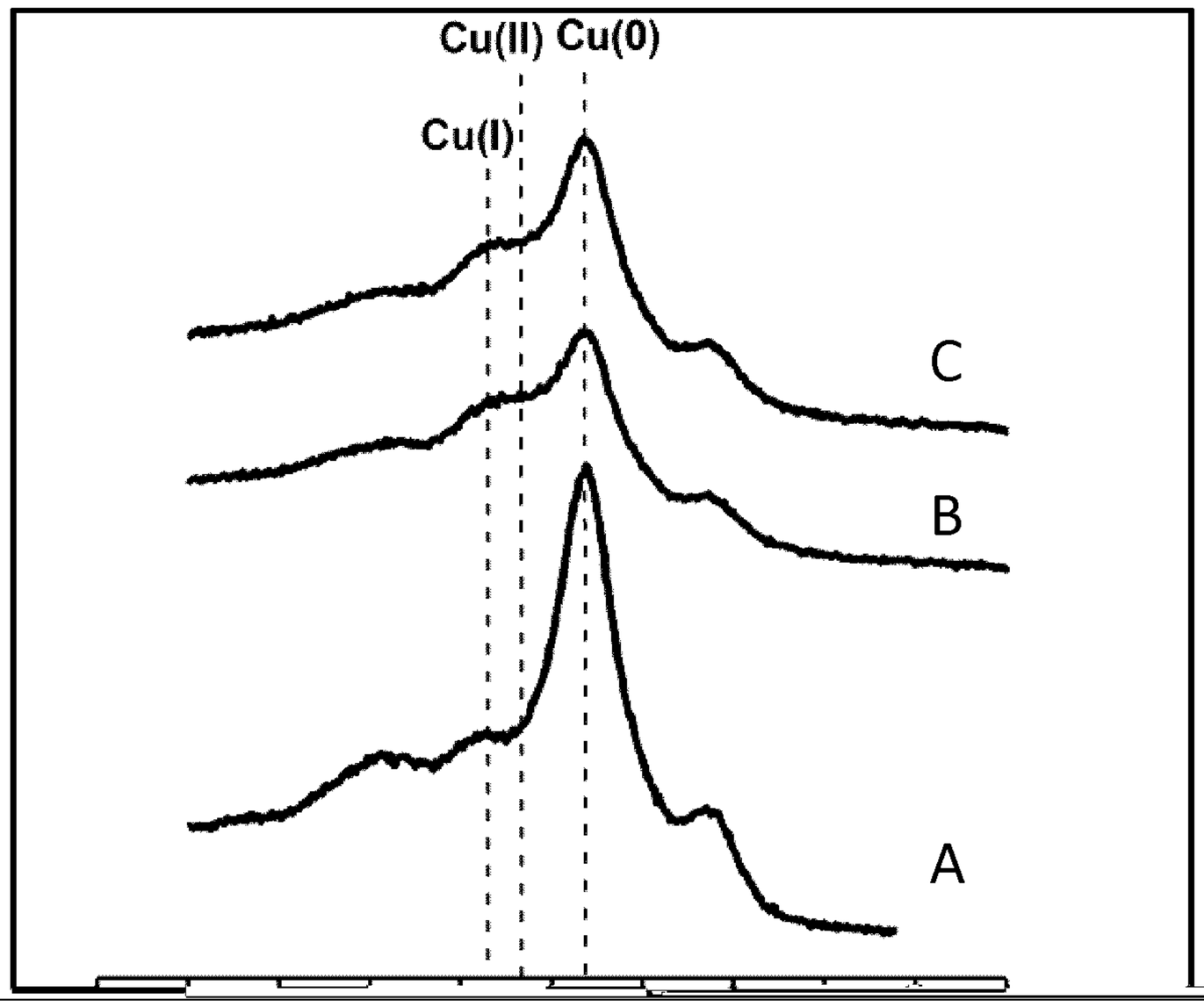
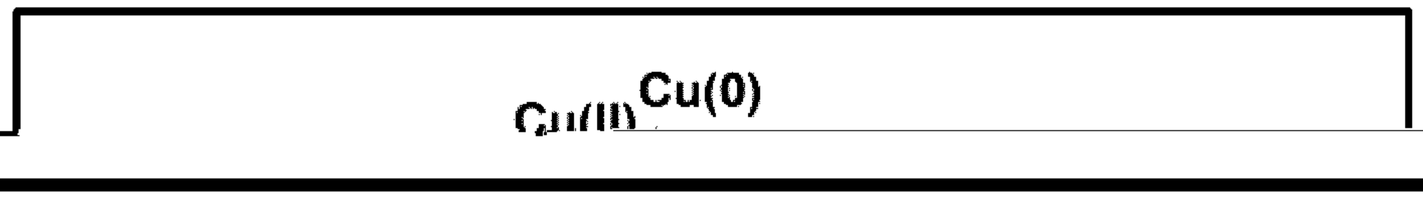
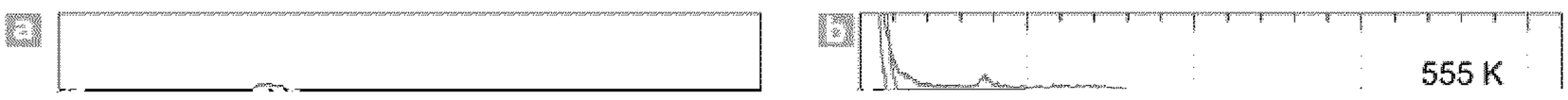

(a)
(b)
Cu(0)
(c)


Cu(II)
Cu(0)
Cu(I)
C
B
A


Cu(II)
Cu(0)


m/z= 28 amu
m/z= 44 amu


m/z=44 amu
oxide as prepared
DTSO NUC/oxide


555 K

ETCHING METAL USING N-HETEROCYCLIC CARBENES

FIELD

The application relates to methods of etching metallic surfaces using compounds that include a N-heterocyclic carbene (NHC).

BACKGROUND

Self-assembled monolayers (SAMs) on metals such as gold have potential application in sensing, electrochemistry, drug delivery, surface protection, microelectronics and microelectromechanical systems, among others. Use of self-assembled monolayers (SAMs) as an interface between metal surfaces and organics has had significant impact on molecular electronics, surface patterning techniques and biosensing (R. G. Nuzzo et al., *J. Am. Chem. Soc.* 105, 4481-4483 (1983), C. D. Bain et al., *J. Am. Chem. Soc.* 111, 321-335 (1989), and J. C. Love, et al., Chem. Rev. 105,

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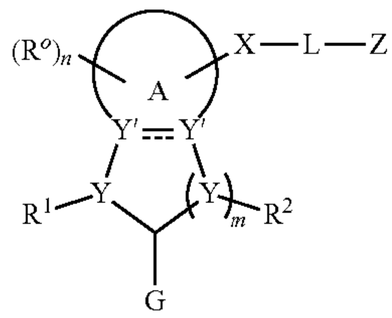
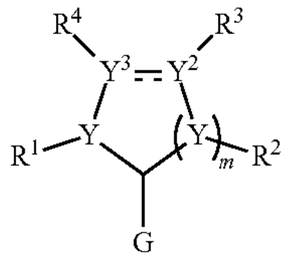
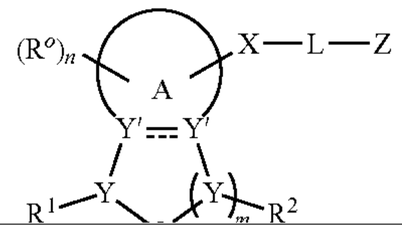
(III)



(IIIa)



(IV)



bene (NHC)-based SAMs with high chemical and electro-

(IVa)

chemically derivatizable group, such as hydroxyl
(OH azide carboxylic acid carbonyl chloride

where two different ordered oxide structures can be observed with high resolution.

FIG. 7g shows an STM image (140 nm×140 nm) of the

dimethyl NHC at 300 K, where residual oxidized regions

butyl and 2-ethyl-1-butyl, 1-heptyl and 1-octyl. As used herein the term "alkyl" encompasses cyclic alkyls, or cycloalkyl groups.

aromatic, saturated or partially saturated, monocyclic, bicy-

heteroaryls, as defined above. Also included within this term are monocyclic and bicyclic rings that include one or more double and/or triple bonds within the ring. Examples of 3-

aziridinyl, oxiranyl, thiiranyl, azirinyl, diaziridinyl, diaziri-

sterically stabilized by substituents adjacent to the carbene. A non-limiting example of such a stabilized carbene is provided below:

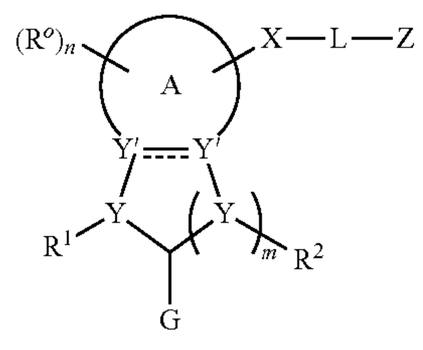
include, but are not limited to, transistors, capacitors, inductors, resistors, diodes, insulators, conductors or combinations thereof.

As used herein, the term "surface properties" refers to properties imparted to a surface as a result of being func-

1,3-diisopropyl-1H-benzo[d]imidazol-3-ium iodide.

As used herein, the term "2a" refers to 1,3-dihydro-1,3-bisisopropylbenzimidazol-2-ylidene), see structural formulae in Example 14.

As used herein, the term "3a" refers to 1,3-diisopropyl-



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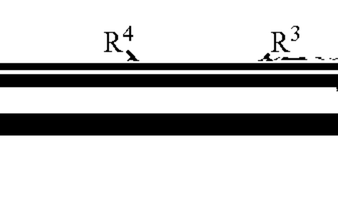


(IIIa)

are connected to form a cycle, or heterocycle, each of which is optionally substituted;

R^3 and R^4 are independently H, halogen, the substituent X-L-Z as defined for Formula II, C_1-C_{10} alkyl, C_{10}-C_{20} alkyl, C_1-C_{10} alkenyl, C_{10}-C_{20} alkenyl, C_1-C_{10} alkynyl, C_{10}-C_{20} alkynyl, C_1-C_{10} alkoxyl, C_{10}-C_{20} alkoxyl, C_3-C_{20} cyclic aliphatic, aryl, heteroaryl, ether, thioether, amine, polyamine, polyether, or polythioether, each of which is optionally substituted; or, any one of R^3 or R^4, with any one of R^1 or R^2, together with the

salt (3a). Results are tabulated in Tables 1 and 2.

Referring to FIG. **1**A, notably, trace (1) shows strong

embodiments, a carbene oxide compound could then be adsorbed onto the clean surface. In other embodiments, a

(I) species was present. Upon exposure to either 2a or 3a, the relative intensity of the Cu Auger peak was reduced.

pattern is shown of the Cu(111) surface after creation of the surface oxide. The multiple diffraction spots observed pro-

[illegible] (11b) (274.1 mg, 1 mmol) in [illegible] at room temperature as an off-white powder (1.20 g, 78% yield).

Example 2(ii). Etching of Metal Oxide and/or Metal Surface

Carbenes were allowed to etch and/or were allowed to

Deposition of dibenzylNHCs onto Oxidized Cu(111) in UHV

1,3-dibenzyl-1H-benzo[d]imidazol-3-ium hydrogen carbonate was deposited via vapor deposition in UHV onto

oxidized copper substrates using the following deposition

UHV

FIG. 7*a* shows TPD spectra following the exposure of

Binding energies of Cu(2p), O(1s), C(1s), and

following a saturation exposure of dimethyl NHC at 300 K. 5

Cu(LMM) for various Cu samples

TABLE 3A-continued

Mass spectrometry results from Cu testing, compounds and their molecular weight detected by mass spectrometry

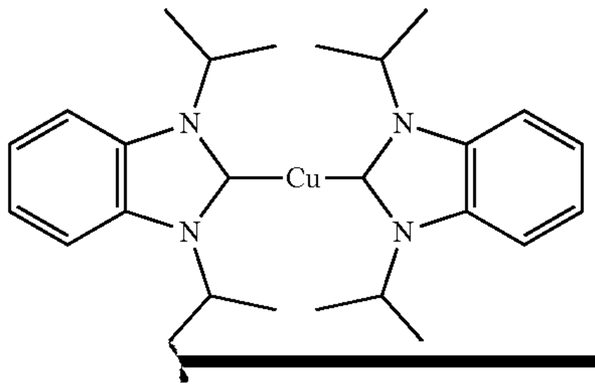
Compound	Molecular weight
	467.27

TABLE 3B

Mass spectrometry results from W testing, compounds and their molecular weight detected by mass spectrometry

Compound	Molecular weight

TABLE 4-continued

Structural Formulae of Compounds that include N-Heterocyclic Carbene

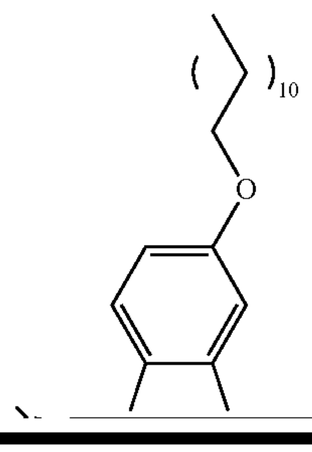
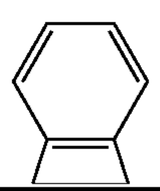
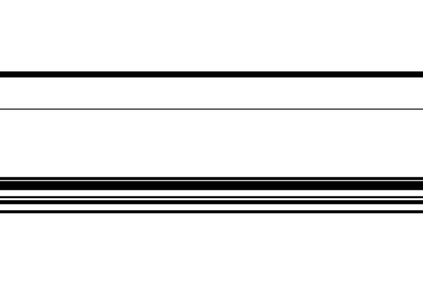
Nickname	Name	Structure
(1d)	5-(Dodecyloxy)-1,3-diisopropy1-1H-benzo[d]imidazol-3-ium iodide	
(2a)	1,3-Dihydro-1,3-bisisopropy1-2H-benzimidazol-2-ylidene	

TABLE 4-continued

Structural Formulae of Compounds that include N-Heterocyclic Carbene

Nickname	Name	Structure
dibenzylNHC	1,3-dibenzyl-1H-benzo[d]imidazol-3-ium hydrogen carbonate	

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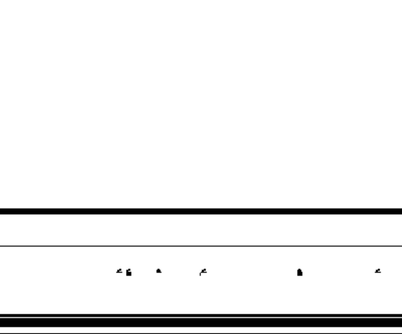

(VI)

wherein:

We claim:

1. A method of etching metal oxide from a metallic

matic ring, a fused aromatic ring system, a heteroaromatic ring, and/or a fused heteroaromatic ring sys-

ring, a fused heteroaromatic ring system, an organometallic complex, a transition-metal catalyst, a metal-oxide catalyst, a simple sugar, a complex sugar, a carbohydrate, or a chemically derivatizable group, OH, azide, carboxylic acid, carbonyl chloride, anhydride, ester, aldehyde, alcohol, amine, halogen, epoxide, thiirane, aziridine, amino acid, nucleic acid, alkene, alkyne, conjugated diene, thiol, or thioester,

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