RESEARCH ON A HIGH PERFORMANCE MULTILAYER ZnO VARISTOR AND ITS FABRICATION WITH WATER BASED TAPE CASTING

WANG LANYI

DOCTOR OF PHILOSOPHY
CITY UNIVERSITY OF HONG KONG
APRIL 2010

CITY UNIVERSITY OF HONG KONG
香港城市大學

Research on a High Performance Multilayer ZnO Varistor and Its Fabrication with Water Based Tape Casting
高性能多層氧化鋅壓敏電阻器及其水基流延工藝的研究

Submitted to
Department of Physics and Materials Science
物理及材料科學系
In Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
哲學博士學位

by

Wang Lanyi
王蘭義

April 2010
二零一零年四月

Abstract

With the rapid development of small size, low working voltage and high reliability of electronic products, the demands for multilayer chip varistors (MLV) which are designed for surge protection and electrostatic discharge (ESD) protection in circuits are increasing rapidly and the requirements for the MLV's properties become stricter. In order to meet the demands of "green" production methods in an environmental protection modern world, it is important to study environmentally friendly water-based (aqueous) tape casting and the replacement of solvent-based (non-aqueous) tape casting with aqueous tape casting. In this study, using chemically synthesized doped zinc oxide (CS powder) as the starting powder, high performance multilayer ZnO varistors were prepared with water-based tape casting.

For the first time, high performance multilayer ZnO varistors were successfully fabricated using both water-based tape casting and a chemically synthesized compound powder. The MLVs made by water-based tape casting exhibit better electrical properties than those made using the solvent-based tape casting. Water-based tape casting reduces MLV's production costs and reaches the goal of environmentally friendly green production, resulting in great social and economic benefits.

The electrical properties of MLVs made by CS powder were compared with those made by metal oxide powder (MO powder). The effect of sintering temperature on the electrical properties of MLVs was studied. With the help of microstructure analysis and electrical property measurement of the MLVs, the MLVs made by CS powder display superior electrical properties as a result of their uniform microstructure throughout. The optimal sintering temperature range for our MLVs is 950℃~1050℃.

Water-based tape casting process was studied. The influence of a water-soluble binder and dispersant on the tape casting slurry was analyzed. The aqueous slurry with shear thinning rheological behavior which was desirable for tape casting was successfully developed by the optimization study of slurry composition. The aqueous

slurry could be stabilised electrosterically by the dispersant. The MLV green sheets were successfully made with water-based tape casting.

Water-based tape casting process was compared with solvent-based tape casting. The microstructure and electrical properties of the MLVs made by water-based tape casting were also compared with those made by solvent-based tape casting. The aqueous green tape is denser than the non-aqueous one. The multilayer ZnO varistors prepared by aqueous tape casting display better electrical properties than those prepared using non-aqueous tape casting. We believe that these superior electrical properties are a direct result of the well dispersed and stable slurry with a shear thinning rheological behavior, which makes dopants distribute more uniformly throughout the MLVs. We conclude that water-based tape casting can replace solvent-based tape casting for the manufacture of high performance multilayer ZnO varistors considering MLV production costs and protection of the environment.

Table of Contents

List of Symbols and Abbreviations

MLV	Multilayer Varistor
MLCV	Multilayer Chip Varistor
MOV	Metal Oxide Varistor
VDR	Voltage Dependent Resistor
TVS	Transient Voltage Suppressors
ESD	Electrostatic Discharge
MLVF	Multilayer Feedthrough Varistor
MLCC	Multilayer Ceramic Capacitor
EMC	Electromagnetic Compatibility
EMI	Electromagnetic Interference
dc	Direct Current
ac	Alternating Current
ε	Relative Permittivity
ε_0	Permittivity of Free Space
SIMS	Secondary Ion Mass Spectroscopy
I	Current
$U(V)$	Voltage
R	Resistance
V_B	Breakdown Voltage
a	Nonlinear Coefficient
I_L	Leakage Current
V_C	Clamping Voltage
C	Capacitance
I_P	Peak Current
E_T	Transient Energy
V_{RMS}	Root Mean Square Voltage
EIA	Electronic Industries Association

IC	Integrated Circuit
SEM	Scanning Electron Microscope or Scanning Electron Microscopy
TEM	Transmission Electron Microscope or Transmission Electron Microscopy
EDS	Energy Dispersive Spectrometer
USB	Universal Serial Bus
LIN	Local Internet
PET	Mylar
PVA	Polyvinyl Alcohol
PVB	Polyvinyl Butyral
PVC	Polyvinyl Chloride
LOM	Laminated Objective Manufacturing
PAA	Polyacrylic Acid
PTC	Positive Temperature Coefficient
Ni-MLCC	Nickel Electrode Multilayer Ceramic Capacitor
ζ	Zeta Potential
TGA	Thermogravimetric Analysis
JEOL	Japan Electron Optics Laboratory Co. Ltd
IEP	Isoelectric Point
EDAX	Energy Dispersive Analysis of X-Ray
PEG	Polyethylene Glycol
XRD	X-Ray Diffraction
CS	Chemical Synthesis
MO	Metal Oxide
PCF	Pharmacie Centrale de France
D_{50}	Powder Mean Particle Size
HEBM	High Energy Ball Milling
PEI	Polyethylene Imine
WEEE	Waste Electrical and Electronic Equipment

RoHS	Restriction of the use of certain Hazardous Substances in Electrical and Electric Waste
EDS	Evaporative Decomposition of Solutions (method)
PPG	Polypropylene glycol
FTIR	Fourier Transform Infrared Spectroscopy
SSPM	Scanning Surface Potential Microscopy
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
DTA	Differential Thermal Analysis
ZMT	$Zn_{0.9}Mg_{0.1}TiO_3$
DLVO	Derjaugin,Landau, Vervey and Overbeek
IEEE	Institute of Electrical and Electronics Engineers
VCC	Voltage Common Cathode
VMOS	Vertical Metal Oxide Semiconductor
MOSFET	Metal Oxide Semiconductor Field-Effect Transistor
SCR	Silicon-Controlled Rectifier
TTL	Transistor-Transistor Logic
PC	Personal Computer
PDA	Personal Digital Assistant
ABS	Anti-lock Braking System
DVD	Digital Versatile Disc
DTV	Digital Television
DVC	Digital Video Cassette
DSC	Digital Still Camera
LCD	Liquid Crystal Display
I/O	Input/Output
SMT	Surface Mount Technology
RFI	Radio Frequency Interference