CHAPTER I
INTRODUCTION

Carbonaceous structures in tubular form, called carbon filaments, were first observed when electron microscopes came into wide use around 1950 (Tibbetts, 1984). In the early 90s, such filaments were observed with a diameter in the range order of the nanometer (Iijima, 1991) and have then been called carbon nanotubes. These first observed multi-walled carbon nanotubes (MWNTs) were grown in an arc-discharge process. Two years later, single-walled carbon nanotubes (SWNTs) could be grown by laser-ablation. At the same time, the catalytic chemical vapor deposition (CCVD) method was first used to grow carbon nanotubes. Because of the peculiar electronic transport properties of the SWNTs (Hamada *et al.*, 1992; Odom *et al.*, 1998) and the high conducting properties of the MWNTs (Poncharal *et al.*, 2002), carbon nanotubes arouse great interest in the microelectronics community and hope for new functional electronic devices (Tans *et al.*, 1998; Javey *et al.*, 2003; Luyken *et al.*, 2003). The attraction and development of CCVD for growing carbon nanotubes by the scientific community can be partly explained by the fact that it is very familiar with CVD techniques. However, the ability to grow carbon nanotubes directly on a substrate at a desired position is a great challenge from a technological point of view. This control over the CCVD growth of carbon nanotubes would permit the integration of the carbon nanotube growth into fabrication processes of microelectronic circuits since the CCVD process requires much lower temperatures than the arc-discharge and laser-ablation processes. The CCVD methods thus seem to be more adapted for large-scale production at lower cost (Cheng *et al.*, 1998; Resasco *et al.*, 2002). This explains why many research groups in the whole world are working on the growth of carbon nanotubes by CCVD.

The CVD process on a supported catalyst consists of several steps. The first is to prepare metal nanoparticles on a substrate. The substrate is then placed in a furnace and the nanoparticles are then generally submitted to a reduction treatment upon heating under typically H_2 or NH_3. Subsequently, hydrocarbon gas or CO is let into the furnace and carbon deposition occurs by catalytic decomposition of the carbon-containing molecules on the metal nanoparticles by temperatures ranging roughly from 500 to 1200 °C. However, the role of the catalyst, on the formation of carbon nanotubes, is more complex. In many cases, hydrocarbon molecules will decompose without forming carbon nanotubes, as has been found for example by Sen *et al.* (1997) who studied the decomposition by pyrolysis of benzene and/or metallocene. Therefore, only a number of catalysts are suitable for carbon nanotubes production. In this research, a novel catalyst, Co-Re/SiO_2, was prepared to synthesize the SWNTs. In addition, this research also compared the quantity and quality of the carbon nanotubes that was obtained by decomposition of CH_4 or CO over a variety of catalyst formulations.

Although the CCVD method is regarded as a promising way for the production of SWNTs, the residue catalyst substrate seems to be a major impurity for some applications that require high SWNT purity. Several methods have been developed to purify the as-prepared SWNTs such as oxidation, acid treatment and micro filtration. A concentrated strong acid, that is difficult to handle, such as HF may be used in the acid treatment while fouling by SWNT cake may reduce the separation efficiency in the micro filtration. A froth flotation process is thus applied to separate the SWNTs from the residue catalyst substrate and to improve the SWNT purity. Froth flotation is a surfactant-based separation process that was widely used to separate hydrophobic particles from hydrophilic particles using air bubble. The aim of this research is to separate the hydrophobic SWNTs from the hydrophilic SiO_2 support in a spent Co-Mo/SiO_2 catalyst.

By applying froth flotation to separate carbon black from a mixture of carbon black and silica as a preliminary study, the froth flotation on the SWNT sample was further studied based on the information of operating conditions obtained from the carbon black study.